PROCEEDINGS

OF THE

NATIONAL ACADEMY OF SCIENCES

INDIA

1959

Vol. XXVIII SECTION - A Part III

NATIONAL ACADEMY OF SCIENCES, INDIA

ALLAHABAD

THE NATIONAL ACADEMY OF SCIENCES, INDIA

(Registered under Act XXI of 1860)

Founded 1930

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STUDY OF THE INFLUENCE OF CONCENTRATION OF SUCROSE ON THE ACETONE-BUTANOL FERMENTATION BY DIFFERENT STRAINS OF CLOSTRIDIUM

By

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[Received on 13th May 1959]

ABSTRACT

The high concentration of sucrose in the culture medium is unfavourable for the formation of butanol or acetone with the various Clostridium tested. The low concentration of 5% gives better yield of butanol and acetone, the increase in concentration of sucrose causes increased sugar consumption without corresponding increase in acetone, butanol or acid production. The formation of acids is not very much influenced by the consumption of sucrose but as the sugar consumption is increased several times the percentage yield of acid becomes low. The increase of concentration not only quantitatively decreases the production of the solvents but their formation is completely inhibited if the sugar consumption is very much increased.

The production of butanol is drawing the attention of scientists all over the world because of its recent use in the production of plastic and rubber like material. A number of micro-organisms have been studied which on growing in carbohydrate substrate produce butanol together with acetone as the chief metabolites and also iso-propyl alcohol, methyl and ethyl alcohal and several volatile and non-volatile acids in smaller quantities. The clostridium fermentation, producing butanol is getting more prominence as compared to the bacterial fermentation or butanol because of the great ease in its manipulation (1) and the high concentrations of sugar solution which can be fermented giving good butanol yield which is the most

important factor in using the fermentation on industrial basis. The influence of mitrogenous sources on the fermentation of butanol and acetone in the culture media has been investigated (2). It has been reported that sucrose concentrations, a little less than 10% is good for the production of butanol and acetone but this can be greatly influenced by the quantity of the nitrogenous food in the culture medium, Kawano (3) has investigated the influence of sucrose concentrations in culture medium between 4·75% to 6·25% and has reported that there is not much difference in the production of butanol between these concentrations.

The concentration of sucrose in the culture probably influences the ratio of the acetone metabolities formed (4). Asai & Haivda have reported that an increase of sugar concentration of the culture medium from 5·26% to 7% increases the fermentation by clostridium no. K M. but it does not increase the yield correspondingly.

Here in this paper the influence of increase of sucrose concentration in the culture media of various strains of Clostridium has been investigated using purely synthetic media, devoid of any vitamines or growth promoting factors. It has been observed that the yield of butanol and acetone is better in low concentration of sucrose in the medium. The increase of the concentration of sugar causes greater consumption of sugar without corresponding increase in the yield of butanol or acetone.

EXPERIMENTAL

Culture media containing the following mineral nutrients were prepared.

Ammonium sulphate	...	0·34 gms.
Magnesium sulphate	...	0·16 gms.

The quantity of sucrose as mentioned in the tables was added and the pH of each culture medium was adjusted to 6·4 by using the requisite quantities of buffer of mono potassium di-hydrogen phosphate and sodium hydroxide, and the total volume of each culture medium was made upto 200 ml.

Culture media were sterilized at 15 lbs. pressure for 30 minutes in autoclave. The media were incubated at room temperature (35°C) for 24 hours and then again sterilized as described above. On cooling they were seeded separately with an active seed culture of the following organisms.

(1) Clostridium butyricum (Frolund), Alfred, Jorgensen Laboratory, Copenhagen.

(2) Clostridium butyricum. 6084, England.

(3) IZ. (561) ATCC (10132) Clostridium aceto-butylicum IZ. m. 16 (Institute Zimotecnico) microbiologia.

(4) IZ. (568) ATCC. (6013) Clostridium pasteurianum IZ m. 16 (Institute Zimotecnico) microbiologia.

(5) IZ. (380) IAL (15-152) Clostridium butylicus IZ. m. 16 (Institute Zimotecnico) microbiologia.

(6) NRRL B. 27 Clostridium acetobutylcium, Illinois.

(7) NRRL. B. 598 Clostridium pasteurianum, Illinois.

(8) NRRL. B. 592, Clostridium butylicus, Illinois.

These cultures were kept at 35°C in an incubator for fermentation. The cultures were analysed after 20 days for the following :—

(1) *Reducing sugar*—10 c.c. of the culture medium were made upto 50 ml. and the solution was titrated against previously standardised Fehling's solution employing methylene blue as indicator near the end point.

(2) *Total sugar*—10 c.c. of the culture medium were hydrolysed with 2 c.c. of dilute hydrochloric acid and after cooling the solution was neutralized by sodium hydroxide and the whole solution was made upto 50 ml. This solution was titrated against previously standardised Fehling solution as described above.

(3) *Acidity*—5 ml. of culture medium were titrated against N/10 sodium carbonate solution using methyl red as indicator.

(4) *Volatile acid*—5 ml. of culture medium were taken into a 100 ml. distilling flask, and 20 ml. of distilled water were added. The solution was distilled collecting the distillate in a known volume of standard N/10 sodium carbonate solution. Excess of sodium carbonate was titrated against standard hydrochloric acid using methyl red as indicator. Thus the amount of sodium carbonate which was reacted by the volatile acid can be calculated.

(5) *Acetone*.—The quantity of acetone was estimated by the method of Messinger. 5 ml. of culture medium were taken into an Iodine flask, to this 50 ml. of distilled water were added. To it 50 ml. of normal caustic soda solution and then 50 ml. of standard (0·2 N) iodine solution were added, from a burette very slowly and with constant stirring. After waiting for 5 minutes (to complete the reaction of iodine with acetone) 50 ml. of normal sulphuric acid were added to this mixture. The mixture was then made acidic by the addition of dilute acetic acid and the unreacted iodine was titrated against a previously standardised hypo solution using starch as the indicator near the end point. The amount of acetone was calculated by the following equation :

Messinger suggested an iodimetric procedure for the following equation :—

$$CH_3COCH_3 + 3I_2 + 4\ NaOH \rightarrow CHI_3 + CH_3COONa + 3H_2O + 3\ NaI \quad (6)$$

(6) *Butyl alcohol* :—5 ml. of culture medium were taken into a 100 ml. distilling flask, to this 10 ml. of distilled water. 25 ml. of 2 N potassium dichromate solution and 10 ml. of dilute sulphuric acid were added and the whole solution was distilled to 2/3 of its volume. Butanol disllitate (in the form of butyric acid) was trapped into a known volume of standard sodium carbonate solution and the unreacted sodium carbonate solution was titrated against a previoudy standardised hydrochloric acid solution using methyl orange as indicator. Knowing the volume of sodium carbonate which has reacted with butyric acid, the amount of butanol was calculated (7).

(7) *Living cells*—25 ml. of the culture medium were taken and to this 10 ml. of 0·001 N potassium dichromate solution was added. It was kept for two hours. In another flask 25 ml. of the culture medium was boiled for two minutes and cooled to room temperature, and 10 ml. of the same potassium dichromate solution were added to it. After two hours both the solutions were titrated against a standard solution of sodium thio-sulphate with starch as indicator. The difference in the two readings gave the amount of sodium thio sulphate in excess which was reacted with the dichromate solution and thus the amount of potassium dichromate which was used by living cells was calculated. This gives an idea of the living cells which are present in the culture.

OBSERVATIONS

The culture media of the experiment were analysed after 20 days and the results tabulated below are expressed per 100 ml. of the culture media.

TABLE 1

Sugar consumption and acid formation by different Butanol Fermenting organisms in culture media containing 5% sucrose as the source of carbon food.

S. No.	Name of organisms	Reducing sugar left in grams	Total sugar left in grams	Sugar consumed in grams	Grams of sodium carbonate required to neutralise total acid
1	Clostridium butyricum Frolund (*a*)	negligible	3·484	1·516	0·1802
2	Clostridium butyricum 6014, England (*b*)	2·719	3·525	1·465	0·1590
3	IZ. (561) ATCC (10132) Clostridium aceto-butylicum IZm 16 (*c*)	negligible	3·561	1·439	0·1166
4	IZ. (563) ATCC. (6013) Clostridium pasteurianum IZm. 16 (*d*)	2·632	3·867	1·330	0·1272
5	IZ. (380) IAL. (15-152) Clostridium butylicus IZm. 16 (*e*)	3·807	4·759	0·241	0·1060
6	NRRL. B. 527. Clostridium acetobutylicium (*f*)	3·712	3·807	1·193	0·1272
7	NRRL. B. 598 Clostridium pasteurianum (*g*)	2·661	3·666	1·334	0·1272
8	NRRL. B. 592 Clostridium butylicus (*h*)	negligible	4·125	0·875	0·2014

TABLE 2

Volatile acid, acetone and butanol formation in culture media containing 5% of sucrose

Serial number	Name of organisms	Gm. of sodium carbonate to neutralise volatile acid	Grams of acetone formed	Percentage of acetone on the basis of sugar consumed	Grams of butanol formed	% of butanol on the basis of sugar added
1	Clostridium butyricum (Frolund). Alfred Jorgensen Laboratory (*a*)	0·1706	0·0341	2·24	1·5450	30·90
2	Clostridium butyricum 6084 England (*b*).	0·1102	0·1290	8·80	1·2650	25·30
3	IZ. (561) ATCC (10132) Clostridium acetobutylicum IZ m. 16 (*c*)	0·1134	0·0760	5·28	1·9750	39·50
4	IZ. (563) ATCC (6013) Clostridium pasteurianum IZ m. 16 (*d*)	0·0572	0·0712	6·17	4·1020	82·04
5	IZ (380) IAL (15-152) Clostridium butylicus IZm. 16 (*e*)	0·1409	0·0920	38·16	4·8450	96·90
6	NRRL B (5 & 7) Clostridium acetobutylicum (*f*)	0·0805	0·1004	8·41	2·1020	42·04
7	NRRL. B. (598) Clostridium pasteurianum (*g*)	0·0381	0·1827	13·69	2·4700	49·40
8	NRRL. B(592) Clostridium butylicus (*h*)	0·1367	0·1160	13·20	2·7600	55·20

TABLE 3

Sugar consumption and acid formation in culture media containing 10% sucrose as the source of carbon food.

S. No.	Name of organisms	Reducing sugar left in grams	Total sugar left in grams	Grams of sugar consumed	Grams of sodium carbonate to neutralise total acid
1	Clostridium butyricum (Frolund) Alfred Jorgensen laboratory (*a*)	negligible	4·8580	5·1420	0·2279
2	Clostridium butyricum 6084 England (*b*)	1·6280	8·2500	1·7500	0·1378
3	IZ (561) ATCC (10132) Clostridium aceto-butylicum IZm. 16 (*c*)	2·6050	6·6800	3·3200	0·0901
4	IZ (563) ATCC (6013) Clostridium pasteurianum IZm 15 (*d*)	3·2090	5·0000	5·0000	0·0689
5	IZ. (380), AL (15-152) Clostridium butylicus IZm. 16 (*e*)	5·892	7·500	2·5000	0·1537
6	NRRL B. 527 Clostridium acetobutylicum (*f*)	5·892	8·2500	1·7500	0·0742
7	NRRL B. 598 Clostridium pasteurianum (*g*)	6·0360	7·9800	2·0200	0·0583
8	NRRL B. 592 Clostridium butylicus (*h*)	4·5000	6·1200	3·8800	0·0848

TABLE 4

Volatile acid, acetone and butanol formation in culture media containing 10% sucrose as the source of carbon food

Serial number	Name of organisms	Gram of sodium carbonate to neutralise volatile acid	Grams of acetone formed × 10⁻²	Percentage of acetone on the basis of sugar consumed	Grams of butanol formed	Percentage of butanol in terms of sugar added
1	Clostridium butyricum (Frolund) Alfred Jorgensen laboratory (*a*)	0·1696	0·2890	0·0560	...	...
2	Clostridium butyricum England 6034 (*b*)	0·0795	0·4785	0·2734	1·6303	16·30
3	IZ (561) ATCC (10132) Clostridium aceto-butylicum IZ. m. 16(*c*)	0·1007	0·3383	0·1189	1·6657	16·65
4	IZ (568) ATCC (6013) Clostridium pasteurianum IZ. m. 16(*d*)	0·1378	0·1847	0·0369	2·2775	22·77
5	IZ. (380) IAL. (15-152) Clostridium butylicus IZ. m. 16 (*e*)	0·0954	2·842	1·1360	0·8480	8·480
6	NRRL. B. 527 Clostridium acetobutylicum (*f*)	0·0901	2·558	1·4617	1·1777	11·77
7	NRRL B. 598 Clostridium pasteurianum (*g*)	0·1516	...	...	0·7965	7·96
8	NRRL B. 592 Clostridium butylicus (*h*)	0·1584	...	...	1·3920	18·92

TABLE 5

Consumption of sugar and acid formation in culture media containing 20% of sucrose as source of carbon food.

S. No.	Name of organisms	Grams of reducing sugar left	Grams of total sugar left	Grams of sugar consumed	Grams of sodium carbonate to neutralise total acid
1	Clostridium butyricum (Frolund) Alfred Jorgensen laboratory (*a*)	0·6360	9·5100	10·49	0·1060
2	Clostridium butyricum 6084, England (*b*)	5·6250	9·5100	10·49	0·0636
3	IZ. (561) ATCC (10132) Clostridium acetobutylicum IZm 16 (*c*)	1·6070	9·5100	10·49	0·0742
4	IZ. (563) ATCC (6013) Clostridium pasteurianum IZm 16 (*d*)	1·4910	8·8400	11·16	0·0742
5	IZ. (380) IAL. (15-152) Clostridium butylicus IZm. 16 (*e*)	3·1730	7·7300	12·27	0·0954
6	NRRL B. 527 Clostridium acetobutylicum (*f*)	3·6390	6·1800	13·82	0·1219
7	NRRL B. 598 Clostridium pasteurianum (*g*)	2·3700	7·7300	12·27	0·1272
8	NRRL B. 592 Clostridium butylicus (*h*)	5·1550	8·2500	11·75	0·0848

TABLE 6

Volatile acids, acetone, and butanol formation in culture media containing 20% of sucrose as the source of the carbon food

Serial number	Name of organisms	Grams of sodium carbonate to neutralise volatile-acid	Grams of acetone formed	Percentage of acetone on the basis of sugar consumed	Grms. of butanol formed	Percentage of butanol on the basis of sugar added
1	Clostridium butyricum (Frolund Alfred Jorgensen laboratory (*a*)	...	...	...	...	...
2	Clostridium butyricum 6084, England (*b*)	...	...	...	1·4128	7·06
3	IZ. (561) ATCC (10132) Clostridium aceto-butylicum IZ m. 16 (*c*)	0·1213	0·1618	1·5462	0·5788	2·89
4	IZ. (563) ATCC (6013) Clostridium pasteurianum IZ. m. 16 (*d*)	0·1038	0·1238	1·1093	1·0569	5·28
5	IZ. (380) IAL. (15—152) Clostridium butylicus IZ. m. 16 (*e*)	0·1166	0·2080	1·6951	1·8117	9·05
6	NRRL B. 527 Clostridium acetobutylicum (*f*)	...	...	...	..	...
7	NRRL. B. 598. Clostridium pasteurianum (*g*)	0·1038	0·292	2·3797	0·5284	2·64
8	NRRL. B. 592 Clostridium butylicus (*h*)	0 1219	...	...	0·6291	3·14

DISCUSSION

The concentration of 5% of sucrose in the culture media has been found to be optimum for all the Clostridium varieties investigated so far as the grams of butanol formed in the culture are concerned. The increase of sucrose concentration to 10% causes great increase of sugar consumption in the case of Clostridium butyricum (*a*) (Frolund) and Clostridum pasteurianum (*d*) IZ. (563) ATCC. (6013) and Clostridium butylicus (*h*) IZ. (380) IAL (15-152)

This increase of concentration of sugar increases the sugar consumption to twice in the case of Clostridium acetobutylicum (*e*), IZ. (561) ATCC (10132), Clostridium butylicus (*c*) NRRL. B. 527, and Clostridium pasteurianum (*g*) NRRL. B. 592.

The consumption of sugar is very mildly affected in the case of Clostridium butyricum (*b*) 6084, England, and Clostridium acetobytylicium (*f*) NRRL. B. 598. This increase however is not accompanied by further production of butanol or acetone. In the case of Clostridium butyricum (a) no acetone or butanol is formed if the concentration of sucrose is increased from 5 to 10 per cent.

On further increase of concentration of sucrose in the culture the consumption of sugar is greatly increased in almost all the Clostridium strains under examination. The increase is more pronounced in those strains which do not show greater sugar consumption when the concentration was increased from 5 percent to 10 percent. In all these cases the formation of acetone and butanol is very much decreased and even the acid formation is hindered.

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EFFECT OF SUCROSE ON THE AVAILABILITY OF PHOSPHATIC METERIALS, MIXED WITH A FRENCH SOIL

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(Received on 11th May, 1959)

ABSTRACT

Addition of sucrose (cane sugar) with phosphatic materials to the soil increases the available phosphate. With an increase is available phosphate, decrease in exchangeable calcium of the soil is observed. The sucrose gets oxidised or is utilised by soil-micro-organism to librate CO_2 or produce organic acids which help in solubilizing the insoluble phosphates. The phosphates do not appear to have any marked effect in increasing the oxidation of sucrose because the soil is well supplied with calcium carbonate. Much of the native soil phosphate as well as the added phosphatic materials are made available by wetting and drying phenomenon, When no sucrose is added, thereby supplying the phosphatic requirements of the plants regularly.

The role of organic matter in increasing the availability of phosphates in soils has been discussed by Sieling, Russell and Dalton[1] and Dhar[2]. Powdered rock phosphote in combination with organic materials has been found to benefit crop growth. Basic slag has proved to be a good phosphatic fertilizer for acidic soils. However, some phosphate which is contained in the organic materials is also incorporated in soils as a result of mineralization and it becomes difficult to differentiate between the soil phosphate and the phosphate of the organic materials. The present investigations were carried on, in order to exclude the phosphates from organic combinations by selecting cane sugar (sucrose) as an organic substance, which is free from phosphate. The citric acid soluble phosphates have been determined and the changes in the phosphate amounts taken as an index of availability under laboratory conditions.

EXPERIMENTAL

The soil used in these experiments was a French soil, the chemical analysis of which is given in Table 1. The soil was well powdered, and passed through 80-mesh sieve. 200 grams of the soil were weighed in enamelled dishes of 25 cm. diameter. 1%C, in the form of cane sugar, (containing 42·2%C) was added to each dish. Then different phosphatic materials, previously powdered and passed through 100-mesh sieve, were added containing 0·5% P_2O_5. The contents of the dishes were thoroughly mixed and the amounts of total carbon, available phosphate and exchangeable calcium were determined. To each dish 20% distilled water was added and then they were exposed to artificial light (100W electric bulb). Moisture was added in the dishes daily and stirring done on alternate days in order to facilitate aeration. Control experiments were kept simultaneously containing no cane sugar but only soil and phosphatic materials. All the exposures were kept in duplicate. After 90 days, samples were taken, they were well powdered, ovendried and then the amounts of total carbon, available phosphate and exchangeable calcium were determined. Cane sugar was again added at the rate of 1%C to the proper dishes, and they were

exposed to light as before. After 180 days, samples were taken and the analyses for carbon, available phosphate and exchangeable calcium made.

Total carbon was determined by Walkley and Black's method[3], using 1 gm. of the ovendried samples. Exchangeable calcium was determined by N-NaCl method of Hissink[4] and available P_2O_5 by citric acid method, using 2% solution (compensation for $CaCO_3$ contained in the soil was made, thereby increasing the usual 1% solution to 2%).

5 grams of the samples were shaken with 50 ml. of 2% citric acid solution in conical flasks and kept in contact for seven days with occasional shakings everyday. After 7 days, the amount of P_2O_5 in the filtrate and washings was determined by getting a precipitate of phospho-ammonium-molybdate, freeing the precipitate of acid and then dissolving it in N/10 NaOH.

The exchangeable calcium was determined by preparing first and second leachates with N-NaCl and finding out the amount of calcium by difference.

The phosphatic materials used in these experiments were Algerian rock phosphates, designated as A, B, C, D_1 and D_2, Indian rock phosphates from Trichonopoly and Kudada, Indian basic slag from Tata Steel Works, mono calcium phosphate (B.D.H.), dicalcium phosphare (Kahlbaum), tricalcium phosphate (U.S.A.), ferric phoshate (B.D.H.) and aluminium phosphate (B.D.H.) They were all analysed for their total P_2O_5 contents. The amounts mixed with 200 grams of the French soil were :

Algerian rock phosphate :

A = 3·376 gms.

B = 3·780 gms.

C = 3·000 gms.

D_1 = 2·526 gms.

D_2 = 2·510 gms.

Indian rock phosphates :

From Trichinopoly : 3·95 gms.

From Kudada : 5·22 gms.

Indian Basic slag from Tata = 13·70 grams

Mono calcium phosphate, $CaH_4(PO_4)_2H_2O$ = 1·774 grams.

Dicalcium phosphate, $CaHPO_4$ = 1·853 grams

Tricalcium phosphate, $Ca_3(PO_4)_2$ = 2·57 grams

Ferric phosphate, $Fe PO_4$ = 3·077 grams

Aluminium phosphate, $Al PO_4$ = 2·33 grams

RESULTS

TABLE 1(*a*)

Chemical analysis of the French Soil

Moisture	=	2·300%
Loss on ignition	=	5·764%
HCl-insoluble	=	78·970%
Sesquioxides	=	7·200%
Fe_2O_3	=	2·784%
P_2O_5	=	0·0927%
CaO	=	4·707%
MgO	=	0·905%
K_2O	=	0·812%
Organic P_2O_5	=	0·0046%
Available P_2O_5 (2% Citric acid)	=	0·0228%
Exchangeable calcium	=	17·03 m. e./100 grams.
Total carbonates as $CaCO_3$	=	7·215%
Total carbon	=	1·110%
Total nitrogen	=	0·1246%
pH	=	7·4

TABLE 1(*b*)

P_2O_5 Contents of phosphatic materials used

Algerian rock phosphate	A	=	29·62%	P_2O_5
,, ,, ,,	B	=	26·45%	,,
,, ,, ,,	C	=	33·37%	,,
,, ,, ,,	D_1	=	39·58%	,,
,, ,, ,,	D_2	=	39·78%	,,
Indian rock phosphates				
Trichinopoly		=	25·338%	
Kudada		=	19·15%	
Inorganic phosphates :				
Monocalcium phosphate		=	56·31%	
Dicalcium phosphate		=	53·97%	
Tricalcium phosphate		=	44·30%	
Ferric phosphate		=	32·49%	
Aluminium phosphate		=	42·92%	

TABLE 2

Control experiment

200 grams soil

Period of exposure in days	Total Carbon %	Carbon Oxidised %	Available P_2O_5 %	Increase in P_2O_5 %	Ex. Ca m. e./100	Change in Ex-Ca m. e./100
0	1·0745	...	0·01916	...	17·07	...
90	1·0540	0·0205	0·02941	0·01025	16·30	−0·77
180	1·0146	0·0599	0·02997	0·01081	18·75	+1·68

TABLE 3 (*a*)

200 gram Soil + 0·5% P_2O_5 as Rock phosphate A

0	1·0887	...	0·26512	...	16·58	...
90	1·0540	0·0347	0·28262	0·01750	16·30	−0·28
180	1·0380	0·0497	0·30016	0·03504	19·25	+2·67

TABLE 3 (*b*)

200 grams soil + 0·5% P_2O_5 Rock phosphate A + 1% C as Cane Sugar

0	1·9540	...	0·24689	...	19·64	...
90	1·1400	0·8140	0·26574	0·01885	17·09	−2·55
180	1·1207	...	0·33094	0·08405	17·75	−1·89

TABLE 4(*a*)

200 grams soil + 0·5% P_2O_5 as Rock phosphate B

0	1·0987	...	0·11538	...	17·10	...
90	1·0980	0·0007	0·13781	0·02243	16·58	−0·52
180	1·0146	0·0841	0·14738	0·03200	17·10	+0·0

TABLE 4(*b*)

200 grams soil + 0·5% P_2O_5 as Rock phosphate B + 1%C as Cane Sugar

0	1·9080	...	0·10926	...	18·10	...
90	1·1645	0·7435	0·10976	0·00050	16·32	−1·78
180	1·1000	...	0.13194	0·02268	17·07	−1·03

TABLE 5 (a)

200 grams soil + 0·5% P_2O_5 as Rock phosphate G

Period of exposure in days	Total Carbon %	Carbon Oxdised %	Available P_2O_5 %	Increase in P_2O_5 %	Ex. Ca m. e./100	Change in Ex-Ca m. e./100
0	1·0791	...	0·08590	...	17·07	...
90	1·0601	0 0190	0·11408	0·02818	16·32	-0·75
180	1·0028	0·0763	0·12316	0·03726	17·50	+0·43

TABLE 5 (b)

200 grams Soil + 0·5 P_2O_5 as Rock phosphate C + 1% C as Cane Sugar

0	1·9080	...	0·07527	...	18·06	...
90	1·1521	0·7559	0·11124	0·03597	17·50	-0·56
180	1·1325	...	0·11557	0·04030	18·06	...

TABLE 6 (a)

200 grams Soil + 0·5% P_2O_5 as Rock phosphate D_1

0	1·0830	...	0·04944	...	17·55	...
90	1·0295	0·0535	0·04944	...	16·30	-1·25
180	1·0146	0·0684	0 04820	- 0 00124	17·25	-0·30

TABLE 6 (b)

200 grams Soil + 0·5% P_2O_5 as Rock phosphate D_1 + 1% C as Cane Sugar

0	1·9720	...	0·04041	...	17·07	...
90	1·2028	0·7692	0·04164	0 00123	16·82	-0·25
180	1·0503	...	0·03566	- 0·00475	19·50	+2·43

TABLE 7 (a)

200 grams Soil + 0·5% P_2O_5 as Rock phosphate D_2

0	1·0887	...	0·04041	...	17·22	...
90	1·0866	0·0021	0·03200	- 0·00840	16·58	- 0·64
180	1·0264	0·0623	0·03429	- 0·00612	16·75	-0·47

TABLE 7 (b)

200 grams Soil + 0·5% P_2O_5 as Rock phosphate D_2 + 1% C as Cane Sugar

0	1·9250	...	0·04122	...	19·15	...
90	1·14330	0·7717	0·04140	0·00018	17·85	- 1·30
180	1·10300	...	0·03189	0·00933	17·75	- 1·40

TABLE 8(*a*)

200 gram Soil + 0·5% P_2O_5 as Trichinopoly rock phosphate

Period of exposure in days	Total Carbon %	Carbon Oxidised %	Available P_2O_5 %	Increase in available P_2O_5 %	Ex-Ca m.e./100	Change in Ex-Ca m.e./100
0	1·0667	...	0·19053	...	18·04	...
90	1·0663	0·0004	0·20270	0·01213	18·36	+0·32
180	1·0385	0·0282	0·23423	0·04370	18·75	+0·71

TABLE 8(*b*)

200 gram Soil + 0·5% P_2O_5 as Tri. R. P. + 1% C as Cane Sugar

0	2·0083	...	0·20116	...	19·05	...
90	1·1843	0·8240	0·18188	− 0·01928	18·55	− 0·50
180	1·1440	...	0·19590	− 0·00526	18·50	− 0·55

TABLE 9(*a*)

200 grams soil + 0·5% P_2O_5 as Kudada rock phosphate

0	1·0317	...	0·03461	...	16·57	...
90	1·0318	..	0·03710	0·00249	17·40	+0·83
180	0·9910	0·0407	0·02688	0·00773	17·75	+1·18

TABLE 9(*b*)

200 grams Soil + 0·5% P_2O_5 Kud. R. P. + 1% C as Cane Sugar

0	1·9380	...	0·03028	...	19·80	...
90	1·1598	0·7782	0·03220	0·00192	15·59	− 4·21
180	1·0385	...	0·03213	0·00185	15·60	− 4·20

TABLE 10(*a*)

200 grams Soil + 0·5% P_2O_5 as Basic Slag

0	1·0540	...	0·42333	...	19·05	...
90	1·0500	0·0040	0·37450	− 0·04883	19·30	+ 0·25
180	1·0146	−0·0394	0·42827	+0·00494	19·55	+ 0·50

TABLE 10(*b*)

200 gram Soil + 0·5% P_2O_5 as B. S. + 1% C as Cane Sugar.

0	1·9530	...	0·41052	...	18·80	...
90	1·1083	0·8447	0·43383	0·02330	18·88	+0·08
180	1·1080	...	0·41653	0·00601	18·90	+0·10

TABLE 11(*a*)

200 grams Soil + 0·5% P_2O_5 as $Ca_3(PO_4)_2$

Period of exposure in days	Total Corbon %	Carbon Oxidised %	Available P_2O_5 %	Increase in P_2O_5 %	Ex. Ca m.e./100	Change in Ex-Ca m.e./100
0	1·0347	...	0·32537	...	15·82	...
90	1·0344	0·0003	0·31375	-0·01162	17·07	+1·25
180	1·0340	0·0007	0·28174	-0·04363	18·30	+2·48

TABLE 11(*b*)

200 grams Soil + 0·5% P_2O_5 as $Ca_3(PO_4)_2$ + 1% C as Cane Sugar

0	1·9938	...	0·34626	...	16·57	...
90	1·1222	0·8716	0·29609	-0·05017	18·10	+1·53
180	1·0220	...	0·25720	-0·08906	19·05	+2·48

TABLE 12(*a*)

200 grams Soil + 0 5% P_2O_5 as Ca H PO_4

0	1·0317	...	0·48352	...	15·57	...
90	1·0300	0·0017	0·52313	0·03960	18·10	+2·53
180	1·0218	0·0099	0·50552	0·02200	17·07	+1·50

TABLE 12(*b*)

200 gram Soil + 0·5% P_2O_5 as Ca H PO_4 + 1% C as Cane Sugar

0	2·0220	...	0·48355	...	15·57	...
90	1·1664	0·8556	0·49273	0·00918	17·50	+1·93
180	1·1600	...	0·46350	-0·02005	17·07	+1·50

TABLE 13(*a*)

200 gram Soil + 0·5% P_2O_5 as $CaH_4(PO_4)_2H_2O$

0	1·0730	...	0·48717	...	24·00	..
90	1·0500	0·0230	0·52814	0·04097	19·64	-4·36
180	1·0267	0·0463	0·48463	-0·00254	19·75	-4·25

TABLE 13(*b*)

200 gram Soil + 0·5% P_2O_5 as $CaH_4(PO_4)_2H_2O$ + 1% C as Cane Sugar

0	1·9860	...	0·50985	...	23·25	...
90	1·1958	0·7722	0·52320	0·01335	20·92	-2·33
180	1·1207	...	0·49995	0·00990	19·25	-4·00

TABLE 14 (a)

200 grams Soil + 0·5% P_2O_5 as Fe PO_4

Period of exposure in days	Total Carbon %	Carbon oxidised %	Available P_2O_5 %	Increase in P_2O_5 %	Ex. Ca m. e./100	Change in Ex.-Ca m. e./100
0	1·0680	...	0·46096	...	18·30	...
90	1·0645	0·0035	0·48204	0·02108	16·58	- 1·72
180	1·0500	0·0180	0·46430	0·00334	18·00	- 0·30

TABLE 14 (b)

200 grams Soil + 0·5% P_2O_5 as $FePO_4$ + 1% C as Cane Sugar

0	1·9310	...	0·45540	...	18·62	...
90	1·1222	0·8088	0·49038	0·03498	16·58	- 2·04
180	1·1325	...	0·45114	−0·00426	18·25	- 0·37

TABLE 15 (a)

200 grams soil + 0·5% P_2O_5 as Al PO_4

0	1·0682	...	0·41878	...	18·31	...
90	1·0646	0·0037	0·48513	0·06635	17·40	−0·91
180	1·0600	0·0082	0·40848	0·01030	16·31	−2·00

TABLE 15 (b)

200 grams Soil + 0·5% P_2O_5 as $AlPO_4$ + 1% C as Cane Sugar

0	2·0132	...	0·40938	...	18·05	...
90	1·1221	0·8910	0·44743	0·03805	16·30	- 1·75
180	1·1200	...	0·40602	0·00336	19·05	+1·0

TABLE 16

200 grams soil + 1% C as Cane Sugar

0	2·0244	...	0·02410	...	17·32	...
90	1·1790	0·8454	0·03710	0·01300	17·60	+0·38
180	1·1440	...	0·03399	0·00989	17·62	+0·40

DISCUSSION

A perusal of the foregoing tables clearly shows that practically all the carbon added in the form of cane sugar (sucrose) is oxidised in 90 days. When a further addition of 1% C after 90 days is made, the carbon is again oxidised with the same speed. The addition of phosphatic materials do not appear to enhance the oxidation markedly as is evident from table-16. The carbon of the soil also gets oxidised with time, the phosphates affecting insignificant oxidation here as well. This may be due to the fact that the soil is already well supplied with calcium carbonate.

Even without the addition of any canesugar (sucrose), there is an increase in the amount of available phosphate in all the treatments (soil + phosphatic material), except when D_2, basic slag and $Ca_3(PO_4)_2$, are added after 90 days' of exposure. As the amount of C, which is oxidised in all the cases, is insignificant, the increase in the availability of phosphates is due mainly to the wetting and drying action of distilled water added to each dish daily.

When cane sugar is used as an energy material. a marked increase in the amounts of avilable phosphate is observed except when Trichinopoly rock phosphate and $Ca_3(PO_4)_2$ are mixed with the soil. Primarily, cane sugar is utilised by a number of bacteria to produce a number of organic acids which have either dissolving action on phosphates or have a tendency to form complexes which are more soluble. Also, cane sugar is oxidised photochemically to produce carbon dioxide, thereby producing carbonic acid in the soil, which brings the insoluble or sparingly soluble phosphates into solution.

The changes in the exchangeable calcium as a result of treating the soil with phosphatic materials alone are irregular. With $Ca_3(PO_4)_2$ and $CaHPO_4$, there is an increase because more calcium is available but with $CaH_4(PO_4)_2$ there is a marked decrease. On adding $CaH_4(PO_4)_2$ to the soil, fixation of phosphate takes place which in its turn brings about a marked decrease in exchangeable calcium[5]. In most of the cases, decreases in exchangeable calcium are observed which imply that either the fixation of phosphate has taken place, after a portion of insoluble phosphate has come into solution by wetting and drying, or such complexes, formed which take away the exchangeable calcium of the soil for their formation and they themselves do not contribute any calcium by exchange-process.

On adding cane sugar with the phosphatic materials, decreases in exchangeable calcium are very marked espicially when cane sugar is used in combination with rock phosphate A, B, D_2, Trichonopoly rock phosphate, Kudada rock phosphate, $CaH_4(PO_4)_2$, and $FePO_4$. Marked decrease in available phosphate and corresponding increases in exchangeable calcium clearly differentiate these treatments from others, where increases in available phosphate are observed with decreases in exchangeable calcium. This shows that the cane sugar acts in different manners with different phosphatic materials.

It is, therefore, evident that cane sugar helps in liberating phosphate from the insoluble phosphate combinations, the amount of phosphate liberated depending upon other constituents present in the phosphatic material and the soil. The French soil under consideration is very rich in calcium carbonate, hence any phosphate which is brought into solution by the oxidation products of cane sugar, gets converted into $CaHPO_4$, $Ca_3(PO_4)_2$, or $CaH_4(PO_4)_2$. This conversion depends a great deal on the amount of organic acids or carbonic acid produced and utilised for phosphate dissolution, From Table 11 (*b*), it is clear that $Ca_3(PO_4)_2$.

has a tendency to be less available as time passes on. $CaH\ PO_4$, and $CaH_4\ (PO_4)$ become less available after 90 day.

The powdered rock phosphates have been found to be of great value as phosphatic fertilizers when mixed with organic manures. Basic slag has also proved to be highly suited to acidic soils. Even ferric phosphate has been shown to be available for the crops when used with organic manures. From my observation it is quite clear that cane sugar, which is completely devoid of any combined phosphate, when added with phosphatic materials to the soil, increase the available phosphate, in general. The rock phosphates show the most favourable action as a result of cane sugar in their combination with the soil.

The rock phosphates contain phosphate as $Ca_3\ (PO_4)_2$ together with some $CaCO_3$. The basic slag has a constitution, $(CaO)_5\ P_2O_5\ SiO_2$. The carbon-dioxide or carbonic acid which is formed as a result of the oxidation of cane sugar, acts on rock phosphates and basic slag in the following manner to give phosphates which are more available.

Rock phosphate :

1. $Ca_3\ (PO_4)_2 + H_2CO_3 = 2CaH\ PO_4 + CaCO_3$

2. $Ca_3\ (PO_4)_2 + 2\ H_2CO_3 = CaH\ PO_4 + Ca\ (HCO_3)_2$

Basic Slag :

$$(CaO)_5\ P_2O_5\ SiO_2 + 8\ CO_2 + 6H_2O = CaH_4\ (PO_4)_2 + 4\ Ca\ (HCO_3)_2 + SiO_2$$

The calcium carbonate present in the soil reacts with these solubilized phosphates to produce less soluble phosphates. However, the availability data given in this paper can not be correlated with the field experiments because $Fe\ PO_4$ has been found to be highly available in 2% citric acid solution. They merely point out the increases or decreases in the citric acid soluble phosphates and as citric acid soluable phosphates give an estimate of phosphate available to plants, the results can be of some guidance when used with caution.

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A THEOREM ON GENERALIZED LAPLACE TRANSFORM INVOLVING MEIJER'S G-FUNCTION

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[Read at the 28th Annual Session of the Academy held at the University of Agra on 7th February 1959]

1. Introduction : The Laplace Transform is defined by the convergent infinite integral

$$(1\cdot1)\quad f(p) = p\int_0^\infty e^{-px} h(x)\, dx,\ R(p) > 0$$

R. S. Varma (5) has generalized it in the form

$$(1\cdot2)\quad \phi(p) = p\int_0^\infty e^{-\frac{1}{2}px}\ (px)^{m-\frac{1}{2}} W_{k,m}(px)\, h(x)\, dx,\ R(p) > 0$$

which reduces to (1·1) when $k = -m+\frac{1}{2}$ by virtue of the indentity

$$W_{-m+\frac{1}{2},\, m}(z) \equiv z^{-m+\frac{1}{2}}\, e^{-\frac{1}{2}z}$$

We shall denote (1·2) symbolically as

$$\phi(p) \underset{k,m}{\overset{v}{=\!=}} h(x)$$

and as usual (1·1) shall be represented by

$$f(p) \doteqdot h(x)$$

Here we prove a theorem connecting this generalized transform with the Laplace Transform and utilize it to evaluate some infinite integrals involving Meijer's G-Function.

2. Theorem :

If $\quad \phi(p) \underset{k,m}{\overset{v}{=\!=}} h(x)$

and $\quad f(p) \underset{\sigma,\mu}{\overset{v}{=\!=}} x^{2m-2\mu}\, h(x)$

and $\quad p^{v} f(p) \doteqdot g(x)$

then

$$\phi(p) = \frac{1}{p^{\nu-2m+2\mu}} \int_0^\infty x^\nu \, G^{3,0}_{2,3}\left(x \,\middle|\, \begin{matrix} 0, \frac{1}{2}-m-k+2\mu \\ -\nu, \frac{1}{2}-\sigma+\mu, 2\mu-2m \end{matrix}\right) g\left(\frac{x}{p}\right) dx$$

$R(\nu) > 0$, $R(\sigma - k + m - \mu) > 0$ and

provided the integral involved is convergent.

Proof: We have, Bose (1, p. 84)

If $\phi_1(p) \doteqdot f_1(t)$

$\phi_2(p) \doteqdot t f_2(t)$

and $\phi_3(p) \doteqdot f_3(t)$

then $$\int_0^\infty \phi_1(u)\, \phi_3(u)\, f_2(u) \frac{du}{u} = \int_0^\infty f_1(v)\, F(v) \frac{dv}{v}$$

where

$$\frac{1}{v} F(v) = \int_0^\infty f_3(z)\,(v+z)^{-1}\, \phi_2(v+z)\, dz$$

provided the integrals converge and L. T.'s of $|f_1(t)|$, $|f_2(t)\, \phi_3(t)|$, $|t f_2(t)|$ and $|f_3(t)|$ exist.

Taking (2, p. 294)

$$\phi_2(p) \equiv p^{-\sigma+1} e^{\frac{1}{2}p}\, W_{k,\mu}(p)$$

$$\doteqdot \frac{t^{\sigma-k-1}}{\Gamma(\sigma-k)}\, {}_2F_1\left[\begin{matrix} \frac{1}{2}-k+\mu, \frac{1}{2}-k-\mu \\ \sigma-k \end{matrix}; -t\right] = t f_2(t)$$

we have $p^\nu f(p) \doteqdot g(t)$

$$\therefore \phi_1(p) \equiv p\, \frac{a^\nu (1+p)^\nu f\{a(1+p)\}}{1+p} \doteqdot e^{-t} g\left(\frac{t}{a}\right) = f_1(t)$$

also let

$$\phi_3(p) = \frac{\Gamma(\nu)\, p}{(1+p)^\nu} \doteqdot t^{\nu-1} e^{-t} = f_3(t)$$

Substituting in Bose's Theorem,

We get $$\frac{\Gamma(\nu)\, a^\nu}{\Gamma(\sigma-k)} \int_0^\infty u^{\sigma-k-1}\, {}_2F_1\left[\begin{matrix} \frac{1}{2}-k+\mu, \frac{1}{2}-k-\mu \\ \sigma-k \end{matrix}; -\mu\right] \frac{f\{a(1+u)\}}{1+u} du$$

$$= \int_0^\infty e^{-v} g\left(\frac{v}{a}\right) F(v) \frac{dv}{v}$$

where

$$\frac{1}{v} F(v) = e^{\frac{1}{2}v} \int_0^\infty z^{\nu-1} (v+z)^{-\sigma} e^{-\frac{1}{2}z} W_{k,\mu}(v+z)\, dz$$

Evaluating the integral on the right by the known integral viz.,

[Erdelyi (3, p. 411)]

$$\int_0^\infty x^{\rho-1} (a+x)^{-\sigma} e^{-\frac{1}{2}x} W_{k,\mu}(a+x)\, dx$$

$$= \Gamma(\rho)\, a^{\rho}\, e^{\frac{1}{2}a}\, G^{3,0}_{2,3}\left(a \,\middle|\, \begin{matrix} 0,\ 1-k-\sigma \\ -\rho,\ \frac{1}{2}+\mu-\sigma,\ \frac{1}{2}-\mu-\sigma \end{matrix}\right); \begin{matrix} R(\rho) > 0 \\ |\arg a| < \pi \end{matrix}$$

Hence

$$(2{\cdot}1) \quad \int_0^\infty x^{\nu}\, G^{3,0}_{2,3}\left(x \,\middle|\, \begin{matrix} 0,\ 1-k-\sigma \\ -\nu,\ \frac{1}{2}+\mu-\sigma,\ \frac{1}{2}-\mu-\sigma \end{matrix}\right) g\left(\frac{x}{p}\right) dx$$

$$= \frac{p^{\nu}}{\Gamma(\sigma-k)} \int_0^\infty u^{\sigma-k-1}\, {}_2F_1\left[\begin{matrix} \frac{1}{2}-k+\mu,\ \frac{1}{2}-k-\mu \\ \sigma-k \end{matrix};\ -u\right] \frac{f\{p(1+u)\}}{1+u}\, du$$

$$R(\nu) > 0, \qquad R(\sigma-k) > 0$$

Now Rathie has shown (4, p. 385) that

$$\text{if} \quad \phi(p) \underset{k,\, m}{\overset{v}{=\!=}} h(x)$$

$$\text{and} \quad f(p) \underset{\sigma,\, \mu}{\overset{v}{=\!=}} x^{2m-2\mu}\, h(x)$$

then

$$(2{\cdot}2) \quad \phi(p) = \frac{p^{m+k-\sigma-\mu+1}}{\Gamma(\sigma-k+m-\mu)} \int_0^\infty t^{\sigma-k+m-\mu-1} (p+t)^{-1} f(p+t)$$

$$\times\ {}_2F_1\left[\begin{matrix} \frac{1}{2}-k+m,\ \sigma+\mu-k-m \\ \sigma-\mu-k+m \end{matrix};\ -\frac{t}{p}\right] dt$$

provided that $R(\sigma-k+m-\mu) > 0$ and the integral is convergent.

In (2·1)

$$\text{for } \sigma \text{ write } \frac{\sigma}{2} + m - \frac{3\mu}{2} + \frac{1}{4}$$

$$\text{for } k \text{ write } k - \frac{\sigma}{2} - \frac{\mu}{2} + \frac{1}{4}$$

and $\qquad$ for μ write $m-\frac{\sigma}{2}-\frac{\mu}{2}+\frac{1}{4}$

and then changing u in to $\frac{t}{p}$ we get after a little simplification

$$\int_0^\infty x^\nu \, G_{2,3}^{3,0}\left(x \,\middle|\, \begin{matrix} 0, \frac{1}{2}-m-k+2\mu \\ -\nu, \frac{1}{2}-\sigma+\mu, 2\mu-2m \end{matrix} \right) g\left(\frac{x}{p}\right) dx$$

$$= \frac{p^{\nu-\sigma+k-m+\mu+1}}{\Gamma(\sigma-k+m-\mu)} \int_0^\infty t^{\sigma-k+m-\mu-1}$$

$$ {}_2F_1\left[\begin{matrix} \frac{1}{2}-k+m, \sigma+\mu-k-m \\ \sigma-k+m-\mu \end{matrix} ; -\frac{t}{p} \right] \frac{f(p+t)}{p+t} \, dt$$

so that (2·1) and (2·2) give the theorem under conditions stated.

Examples 1

Taking

$$g(x) \doteqdot x^{\rho-\nu-1} \doteqdot \frac{\Gamma(\rho-\nu)}{p^{\rho-\nu-1}} = p^\nu f(p)$$

$$R(\rho) > R(\nu) > 0$$

so that

$$f(p) = \Gamma(\rho-\nu) p^{1-\rho}$$

Now Rathie (4, p. 382)

$$x^{\nu-1} \underset{k,\,m}{\overset{\nu}{=}} \frac{\Gamma(\nu)\,\Gamma(\nu+2m)}{\Gamma(\nu+m-k+\frac{1}{2})} p^{1-\nu}$$

$$R(\nu) > 0, R(\nu+2m) > 0$$

giving

$$h(x) = \frac{\Gamma(\rho-\nu)\,\Gamma(\rho+\mu-\sigma+\frac{1}{2})}{\Gamma(\rho)\,\Gamma(\rho+2\mu)} x^{\rho+2\mu-2m-1}$$

and

$$\phi(p) = \frac{\Gamma(\rho-\nu)\,\Gamma(\frac{1}{2}-\sigma+\mu+\rho)\,\Gamma(-2m+2\mu+\rho)}{\Gamma(\rho)\,\Gamma(\frac{1}{2}-m-k+2\mu+\rho)} p^{1-\rho-2\mu+2m}$$

Hence $\displaystyle\int_0^\infty x^{\rho-1} G_{2,3}^{3,0}\left(x \,\middle|\, \begin{matrix} 0, \frac{1}{2}-m-k+2\mu \\ -\nu, \frac{1}{2}-\sigma+\mu, 2\mu-2m \end{matrix} \right) dx$

$$= \frac{\Gamma(\rho-\nu)\,\Gamma(\frac{1}{2}-\sigma+\mu+\rho)\,\Gamma(2\mu-2m+\rho)}{\Gamma(\rho)\,\Gamma(\frac{1}{2}-m-k+2\mu+\rho)}$$

$R(\rho-\nu) > 0$, $R(\sigma-k+m-\mu) > 0$, $R(\frac{1}{2}-m-k+2\mu+\rho) > 0$.

which is a particular case of the integral (Erdelyi, 3, p. 418)

$$\int_0^\infty x^{\rho-1}\, G^{m,n}_{p,q}\left(ax \;\middle|\; \begin{matrix} a_1 \ldots a_p \\ b_1 \ldots b_q \end{matrix}\right) dx$$

$$= \frac{\prod_{j=1}^{m} \Gamma(b_j+\rho) \prod_{j=1}^{m} \Gamma(1-a_j-\rho)}{\prod_{j=m+1}^{q} \Gamma(1-b_j-\rho) \prod_{j=n+1}^{p} \Gamma(a_j+\rho)}\, a^{\rho}$$

$p+q < 2(m+n)$ $\qquad -\min R(b_j) < R(\rho) < 1-\max R(a_j)$

$|\arg a| < (m+n-\frac{1}{2}p-\frac{1}{2}q)\pi \quad ; \quad 1 \leqslant j \leqslant m \qquad 1 \leqslant j \leqslant n$

Example 2.

If we take

$$g(x) = x^{2m-2\mu-1}\; {}_{r+2}F_{s\,2}\left[\begin{matrix} \alpha_1 \ldots \alpha_r,\ 2m-2\mu+\nu,\ 2m+\nu \\ \beta_1 \cdot \beta_s,\ 2m-\mu+\nu-\sigma+\frac{1}{2},\ 2m-2\mu \end{matrix} : x\right]$$

so that (2, p. 297)

$$f(p) = \frac{\Gamma(2m-2\mu)}{p^{2m-2\mu+\nu-1}}\; {}_{r+2}F_{s+1}\left[\begin{matrix} \alpha_1 \cdots \alpha_r,\ 2m-2\mu+\nu,\ 2m+\nu \\ \beta_1 \ldots \beta_s,\ 2m-\mu+\nu-\sigma+\frac{1}{2} \end{matrix} : \frac{1}{p}\right]$$

$$\overset{\nu}{\underset{\sigma,\,\mu}{=}}\; x^{2m-2\mu}\, h(x)$$

giving

$$h(x) = \frac{\Gamma(2m-2\mu)\,\Gamma(2m-\mu+\nu-\sigma+\frac{1}{2})}{\Gamma(2m-2\mu+\nu)\,\Gamma(\nu+2m)}\, x^{\nu-1}\; {}_rF_s\left[\begin{matrix} \alpha_1 \cdot \alpha_r \\ \beta_1 \ldots \beta_s \end{matrix} : x\right]$$

[Rathic, 4, p. 383.]

$$\text{and } \phi(p) = \frac{\Gamma(\nu)\,\Gamma(2m-2\mu)\,\Gamma(2m-\mu+\nu-\sigma+\frac{1}{2})}{\Gamma(2m-2\mu+\nu)\,\Gamma(\nu+m-k+\frac{1}{2})}\, p^{1-\nu}$$

$$\times\, {}_{r+2}F_{s+1}\left[\begin{matrix} \alpha_1 \ldots \alpha_r,\ \nu,\ \nu+2m \\ \beta_1 \cdot \beta_s,\ \nu+m-k+\frac{1}{2} \end{matrix} : \frac{1}{p}\right]$$

so that

$$\int_0^\infty x^{\nu+2m-2\mu-1}\, G^{3,0}_{2,3}\left(x \;\middle|\; \begin{matrix} 0,\ \frac{1}{2}-m-k+2\mu \\ -\nu,\ \frac{1}{2}-\sigma+\mu,\ 2\mu-2m \end{matrix}\right)$$

$$\times {}_{r+2}F_{s+2}\left[\begin{matrix}\alpha_1\ldots\alpha_r,\ 2m-2\mu+\nu,\ 2m+\nu\\ \beta_1\ldots\beta_s,\ 2m-\mu+\nu-\sigma+\frac{1}{2},\ 2\mu-2m\end{matrix} : \frac{x}{p}\right]dx$$

$$= \frac{\Gamma(\nu)\ \Gamma(2m-2\mu)\ \Gamma(2m-\mu+\nu-\sigma+\frac{1}{2})}{\Gamma(2m-2\mu+\nu)\ \Gamma(\nu+m-k+\frac{1}{2})}$$

$$\times {}_{r+2}F_{s+1}\left[\begin{matrix}\alpha_1\ldots\alpha_r,\ \nu,\ \nu+2m\\ \beta_1\ldots\beta_s,\ \nu+m-k+\frac{1}{2}\end{matrix} : \frac{1}{p}\right]$$

$$R(\nu) > 0,\ R(2m-2\mu) > 0,\ R(\sigma-k+m-\mu) > 0$$

The author is grateful to Dr. B. R. Bhonsle for his keen interest in the paper.

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INFLUENCE OF PHOSPHATES IN INCREASING PHOTO-CHEMICAL NITROGEN FIXATION IN SOILS

By

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[Received on 3rd January, 1959]

ABSTRACT

When energy rich materials like cow-dung and wheat straw are added to the soils under unsterile and sterile conditions, they undergo oxidation and liberate energy which is utilised in the fixation of nitrogen from atmosphere. The efficiency of nitrogen fixation is more in unsterile condition than in sterile condition. The efficiency of nitrogen fixation increases by the addition of different phosphates.

In recent years Dhar (1) has developed a new aspect of the value of phosphates in the maintenance and improvement of land fertility. He has emphasized that calcium phosphate status of all countries should be raised in permanent agriculture. According to Bear "within limits phosphate fertilizers together with potash salts and lime can be substituted for nitrogen fertilizers. Their use stimulates the nitrogen fixing bacteria both symbiotic and non-symboitic to greater activity. The marked growth of white colover that follows the addition of phosphate and potash resembles the application of nitrogenous fertilizers (2). Hence a study of the effect of mono-calcium phosphate, dicalcium-phosphate, tricalcium phosphate, (all of Analah quality) basic slag (Tata basic slag) on the efficiency of nitrogen fixation in soils in unsterile and sterile conditions was made.

EXPERIMENTAL

The soil used for the experiment was homogenised by passing through a 100 mesh sieve. For the unsterile experiments an amount of oven dried soil was taken in 24 cm. diameter enamel dishes, to which, the energy materials and/or phosphates when added, the total weight of the reacting mixture became 100 gms. Two energy rich materials *viz.* cow-dung and wheat straw were added as 0·5% carbon. The phosphates were added as 0·5% P_2O_5. The sets were exposed to artificial light of 100 watt electric bulb placed at a vertical distance of 2 feet. The moisture content of the system was maintained at 20-25% by adding distilled water. The contents of the plates were thoroughly stirred with a glass rod on alternate days to facilitate aeration. Samples were taken after 240 days, after making it homogenous, and analysed for total carbon (3) and total nitrogen (4).

For the sterile experiments an amount of soil was taken in 40 ml. test tube to which, when energy materials and/or phosphates were added, the total weight of the reacting mixture became 5·00 gms. The doses of carbon and phosphates were same as in unsterile experiments. 10 ml. of distilled water was added and the test tubes were plugged with cotton wool. The test tubes with the contents were now sterilised in an autoclave at a pressure of 15 lbs per square inch for 30 minutes. The test tubes were exposed to same arrangment of artificial light as that of unsterile experiments. Before the estimations the sterile test tubes were evaporated to

dryness after adding few drops of very dilute sulphuric acid in order to avoid the loss of ammonia during drying. The estimation for total carbon and nitrogen was done after 300 days. The whole test tubes along with the dried mass were now broken into a Kjeldahl flask and finally estimated for total carbon and nitrogen as in unsterile experiments.

Few test tubes were tested twice at the end of the period of exposure for the growth of Azotobacter or any other bacterial contamination by the usual plate method and were found to give negative results thus corfirming the sterility of the tubes.

The results are expressed as efficiency of nitrogen fixation (mgm. of nitrogen fixed per gm. of carbon oxidized). The results are recorded below :

TABLE 1

Percentage composition of the soil used :

Silica (HCl insoluble)	81·91
Sesqui-oxides	11·40
Fe_2O_3	5·82
CaO	1·9812
Loss on ignition	4·22
MgO	1·0214
K_2O	0·7032
Total P_2O_5	0·1173
Available P_2O_5	0·0089
Total carbon	0·9417
Total nitrogen	0·0700
Carbon/nitrogen ratio	13·4
(pH)	7·2
Exchangeable Clacium (NaCl method)	10·2 m.e. %

TABLE 2

Percentage composition of Tata basic slag :

Silica	23·66
CaO	34·36
MgO	5·28
K_2O	9·07
Fe_2O_3	11·72
Total phosphate	7·59
Available phosphate (soluble in 1% citric acid)	4·46

TABLE 3

Percentage analysis of Energy Materials used

	Straw	Cow-dung
Ash	11·99	36·53
Loss on ignition	88·00	63·46
Silica	7·0760	30·6600
Calcium Oxide	0·7840	2·520
Magnesium oxide	0·2100	0·9342
Potassium oxide	1·6618	0·7216
Phosphate	0·2925	0·6729
Total carbon	36·69	28·62
Total nitrogen	0·5112	1·0108
C/N ratio	71·78	28·34

TABLE 4

	Unsterile		Sterile	
	Efficiency	% increase in efficiency	Efficiency	% increase in efficiency
Soil + 0·5% carbon as cow dung	49·1	—	22·3	—
Soil + 0·5% carbon as cow dung + monocalcium phosphate	50·5	2·8	22·8	2·2
Soil + 0·5% carbon as cow dung + di-calcium phosphate	59·4	20·9	24·9	11·6
Soil + 0·5% carbon as cow dung + tri-calcium phosphate	52·8	7·5	23·9	7·1
Soil + 0 5% carbon as cow dung + Basic Slag phosphate	52·4	6·7	23·5	5 3

TABLE 5

Soil + 0·5% carbon as wheat straw	49·8	—	24·4	—
Soil + 0·5% carbon as wheat straw + mono-Calcium phosphate	51·8	4·0	25·2	3·2
Soil + 0·5% carbon as wheat straw + di-Calcium phosphate	62·1	24·7	26·4	8·1
Soil + 0·5% carbon as wheat straw + tri-Calcium phosphate	53·5	7·4	25·8	5·7
Soil + 0·5% carbon as wheat straw + Basic-slag	52·8	6·0	25·5	4·5

DISCUSSION

An examination of the above tables clearly shows that the efficiency of nitrogen fixation is always higher in unsterile sets than in the sterile experiments. This is perhaps due to the fact that in unsterile condition bacterial nitrogen fixation is also taking place besides the photo-chemical nitrogen fixation. When the energy rich materials such as cow dung and wheat straw are added on the surface of the soil they are slowly oxidised and liberate energy which is utilised for fixing the atmospheric nitrogen on the surface under suitable conditions. Under natural condition (unsterile) nitrogen is fixed both photochemically and by micro-organism but under sterile conditions only the photo-chemical action is responsible for nitrogen fixation (5).

It is also clear that when different phosphates are added they increase the efficiency of nitrogen fixation. The highest per cent increase in the efficiency of nitrogen fixation by phosphates is observed with di-calcium phosphate. The order of the different phosphates in increasing the efficiency of nitrogen fixation is as follows :

Di-calcium phosphate > Tri-calcium phosphate > Basic slag > Mono-calcium phosphate.

Mono-calcium phosphate is distinctly acidic in reaction and shows a lesser efficiency than $CaHPO_4$, $Ca_3(PO_4)_2$ and basic slag.

The reason for the increase in the efficiency of nitrogen fixation by phosphates is very simple. During nitrogen fixation, nitrogenous compounds like proteins, amino acids and ammonium salts are formed which undergo ammonification and nitrification as a result of oxidation aided by light as follows :—

$$\text{Protein} \xrightarrow{O_2} \text{Amino acid} \xrightarrow{O_2} \text{Ammonia} \xrightarrow{O_2} NO_2 \xrightarrow{O_2} NO_3$$

In this reaction there is always a possibility of formation of easily decomposable substance, ammonium nitrite, which readily breaks into water and nitrogen gas which is lost.

$$NH_4NO_2 = N_2 + 2\,H_2O + 718 \text{ K. Cal}$$

Thus the process of nitrogen fixation is always opposed by the phenomenon of nitrogen loss. Hence the apparent efficiency of nitrogen fixation, *i.e.*, the amount of nitrogen fixed in mgms. per gram of carbon oxidised appears to fall off when ammonification and nitrification occur. But in presence of phosphates there is always the possibility of the formation of more stable phospho-proteins and nucleo-proteins by the combination of proteins and phosphorus compounds. These compounds resist ammonification and nitrification better than proteins alone and therefore the efficiency of nitrogen fixation increases in presence of phosphates than in its absence.

Moreover the decomposition of ammonium nitrite is accelerated by the presence of acids. When organic materials are oxidised, organic acids may be formed which accelerate the decomposition of ammonium nitrite leading to nitrogen loss. But in presence of phosphates which act as buffer, the increase in the hydrogen-ion concentration is not possible. Hence the efficiency of nitrogen fixation is higher in presence of phosphates than in its absence.

Also addition of calcium phosphates and basic slag introduces calcium ions which may form calcium nitrite by reacting with ammonium nitrite. Calcium nitrite being more stable than ammonium nitrite decreases the nitrogen loss with the net result that an increase in the efficiency of nitrogen fixation appears.

MECHANISM OF NITROGEN FIXATION

When cow dung and wheat straw are oxidised on the surface of soil, they liberate large amounts of energy according to the following equation :—

$$C_6H_{12}O_6 = 6\ CO_2 + 6\ H_2O + 676\ \text{K Cal.}$$

The energy thus liberated is much more than the energy required to decompose water molecule into H and OH.

$$H_2O + 112\ \text{K Cal} = H + OH$$

The atomic hydrogen thus formed combines with the molecular nitrogen perhaps adsorbed on the surface of soil and forms ammonia.

$$N2 + 3H_2 \rightleftharpoons 2\ NH_3$$

The ammonia thus formed undergoes oxidation into NO_2^- and NO_3^-.

ACKNOWLEDGEMENT

I am grateful to Prof. N. R. Dhar for his keen interest in guiding the above work.

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ADSORPTION OF CRYSTAL VIOLET BY HYDROUS CHROMIUM OXIDE

PART II. HEAT OF ADSORPTION

By

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[Received on 4th May, 1959]

ABSTRACT

The first paper of this series[1] deals with the nature of adsorption of Crystal Violet by hydrous oxide of chromium. It was noted that the adsorption of Crystal Violet increases with increasing temperature. In the present paper, the heats of adsorption have been calculated from the adsorption isotherms of different samples A, B and C at 30°, 35° and 40°C. The results presented here are for five hours of contact. The following results have been concluded.

1. The whole process of adsorption is endothermal and takes place with adsorption of heat and such cases are rare for the adsorption of gases on solid surface.
2. The process becomes more endothermal with increasing coverage, passes through a maximum and then decreases.
3. The endothermal nature has been explained due to the dissociation of aggregated micelles of the dye to simpler ones, which are mainly adsorbed by the surface.
4. The adsorption is due to active basic group of the dye and may be said to be chemisorption.
5. The actual adsorption process is exothermal and the total heat change observed is the algebraic sum of the heat of adsorption and the heat of dissociation of the dye micelle which is endothermal.

The adsorption isotherms for the adsorption of Crystal Violet dye by three samples A, B and C of hydrous chromium oxide given in Figs. 1, 2 and 3 show that the amount of dye adsorbed per gram mole of Cr_2O_3, increases with increasing temperature. This indicates that adsorption may be endothermic. The nature of the curve which is convex to the concentration axis, also indicates that heat of adsorption is less than the heat of aggregation of Crystal Violet micelle. The results can further be confirmed by calculating the heat of adsroption which have been calculated as follows :—

In an adsorbate and adsorbent system equilibrium is established when the isothermal transfer is established or when the isothermal-transfer of small quantity of gas from the adsorbed phase brings about no change in the free energy of the system *i.e,*

$$\left(\frac{\partial Fg}{\partial n}\right)_T = \left(\frac{\partial Fa}{\partial a}\right)_T$$

When F_g = free energy of gas and is a function n and T

F_a = free energy of adsorbate, is a function of a and T

F_g and F_a can be mesured in calories per c. c. while n and a can be

measured in moles per c. c. On applying second law of thermodynamics, we get :

$$RT^2\left(\frac{\partial \ln P}{\partial t}\right)_a = Q_d + RT$$

on integrating we get

$$\frac{R\,T_1\,T_2}{T_1 - T_2} \ln \frac{p_1}{p_2} = Q \text{ isoteric.}$$

In the present case of the adsorption of the dye

$$\frac{R\,T_1\,T_2}{T_1 - T_2} \ln \frac{C_1}{C_2} = Q, \text{ where } C_1 \text{ and } C_2$$

are the concentrations for the same amount of dye-stuffs adsorbed at temperatures T_1 and T_2. The data given below (Tables 1, 3 and 5) give the values of C_1 and C_2 extrapolated from the adsorption isotherms at temperatures 30°, 35° and 40°C for the same amount of dye adsorbed (Figs. 1, 2 and 3)

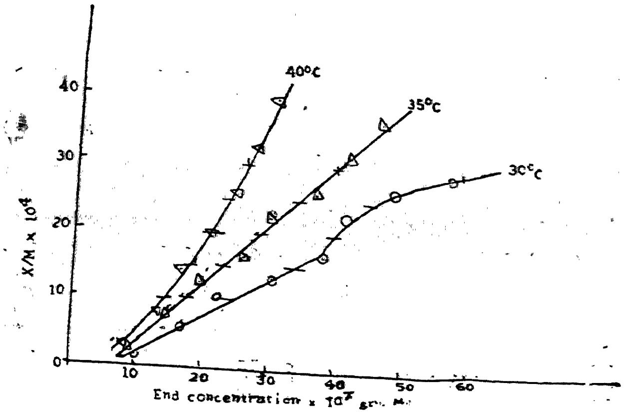


Fig. 1. Adsorption isotherms of crystal violet on hydrous chromium oxide sample A at different temperatures.

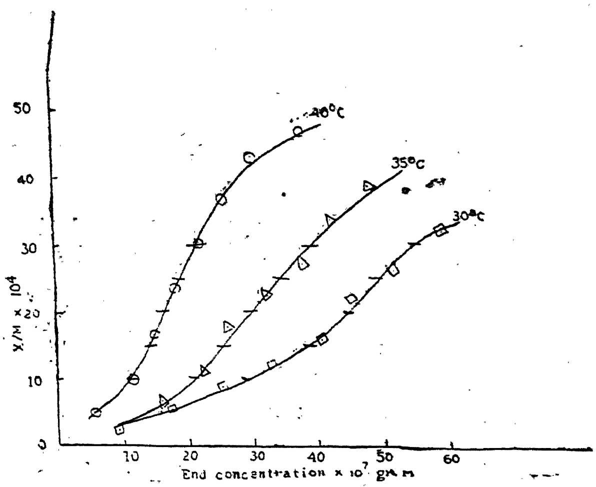


Fig. 2. Adsorption isotherms of crystal violet on hydrous chromium oxide sample B at 30°, 35° and 40°C

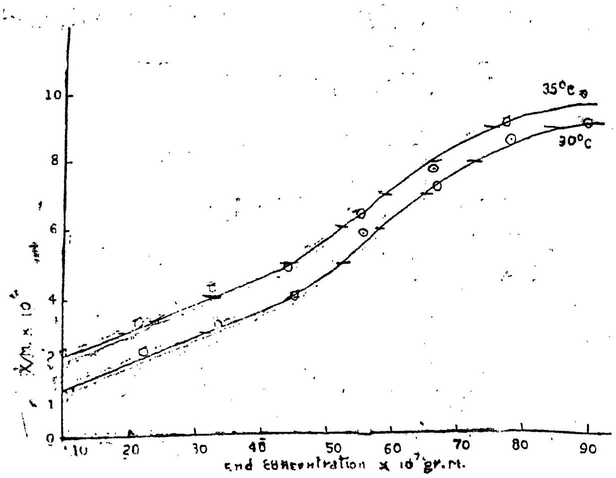


Fig. 3. Adsorption isotherms of crystal violet on hydrous chromium oxide Sample C at 30° and 35°C

TABLE 1

Sample A.

$X/M \times 10^4$	End conc. $C_1 \times 10^7$ at 30°C (T_1)	End. conc. $C_2 \times 10^7$ at 35°C (T_1)	End. con. $C_3 \times 10^7$ at 40°C (T_3)
30	58·5	39·75	26·25
25	45·0	34·0	23·5
20	39·5	28·5	20·5
15	33·5	23·0	17·5
10	24·0	17·5	14·5

TABLE 2

Sample A.

Heat of adsorption.

$X/M \times 10^4$	Q (30°C-40°C) calories	Q (35°-40°C) calories	Q (30° and 35°C) calories	Mean Q calories
30	—15106·9	—15899·06	—14366·17	—15124·0
25	—16582·5	—14152·10	—10394·5	—13709·7
20	—12359·5	—12616·9	—12111·31	—12362·5
15	—12238·3	—10472·9	—13392·48	—12034·5
10	—9495·8	—7199·5	—11718·42	—9471·2

TABLE 3

Sample B.

$X/M \times 10^4$	$C_1 \times 10^7$ at 30°C (T_1)	$C_2 \times 10^7$ at 35°C (T_2)	$C_3 \times 10^7$ at 40°C (T_3)
30	55·0	39·1	21·5
25	49·0	34·5	19·0
20	45·0	30·0	16·2
15	39·5	25·5	14·2
10	28·5	20·7	11·2

TABLE 4

Sampe B. Heat of Adsorption.

$X/M \times 10^4$	Q (30°C-40°C) calories	Q (35°C-40°C) calories	Q (30°C-25°C) calories	Mean Q calories
30	—17706·7	—22922·1	—12657·9	—17762·2
25	—17854·2	—22851·5	—13016·6	—17907·8
20	—19256·04	—23610·3	—15040·9	—19302·4
15	—19282·08	—22428·09	—16236·6	—19315·6
10	—17602·5	—23539·7	—11855·08	—17665·7

TABLE 5

Sample C Heat of adsorption

$X/M \times 10^4$	$C_1 \times 10^7$ at 30°C (T_1)	$C_2 \times 10^7$ at 35°C (T_2)	Q (calories)
9·0	83·5	75·5	—3741·01
8·0	72·7	67·2	—2903·9
7·0	65·2	59·5	—3390·3
6·0	58·5	52·5	—4014·3
5·0	52·7	45·5	—5449·2
4·0	45·4	32·5	—12401·7
3·0	32·0	19·5	—18371·9

From the above data, the heats of adsorption have been calculated and are reproduced in tables 2, 4 and 5 for different samples of hydrous oxide of chromium.

From the results it is found that heat of adsorption is negative. However, the calculated heat of adsorption is significantly large. It should be noted here that the Crystal Violet dye in solution behaves as colloidal electrolyte and the aggregated cation dissociates into simpler units on dilution, so that we have equilibrium,

$$A_n \rightleftharpoons nA$$

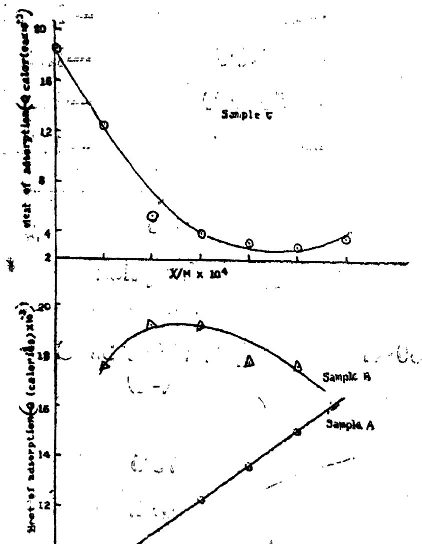
It appears that the adsorption is of chemical nature and is likely to be more prominent for the simpler cations than the aggregated ones. Hence, when adsorption occurs of the simpler cations, the above equilibrium is shifted and more of the aggregated cations dissociate into simpler units. In other words, the adsorption of Crystal Violet cations is followed by the dissociation of the aggregated micelle, so that the total heat calculated includes the heat of dissociation of the aggregated cations. Ordinarily however, the adsorption process is attended with decrease in surface free energy and also a decrease in entropy, the relation being

$$\triangle F^{\circ} = \triangle H^{\circ} - T\triangle S^{\circ}$$

The adsorption process is expected to be always exothermic. In the present case the adsorption of Crystal Violet is

(*i*) connected with the dissociation of the aggregated cations into simpler one and

(*ii*) chemisorption between the adsorbate and the hydrous oxide, possibly preceeded by physical adsorption.



• Fig. 4. Heat of adsorption and amount of crystal violet adsorbed by hydrous chromium oxide. Samples A, B and C.

It is also seen from the Fig. 4 for the amount of dye adsorbed and Q or the heat of adsorption decreases with the increase of the dye adsorbed and passes through

a miximum. Some investigators[2] have reported similar results, though doubts have been expressed about the correctness of their experimental data. The decrease in heat of adsorption with increasing amount of adsorption has been reported in the case of caesium on tungsten[3], oxygen in charcoal[4], ethylene on tantalum[5]. We have however, noted that with hydrous oxide of chromium sample A, the heat of adsorption increases with increasing amount of adsorption. It may be, that this also passes through a maximum for a very concentrated solution of Crystal Violet.

The fall in heat of adsorption may be attributed to two reasons. The one considered by Constable and Taylor[3] is due to surface heterogenity. On a heterogeneous surface, the most active sites will be covered first because adsorption is likely to proceed more rapidly on them. Even if there has been random coverage initially there will be subsequent spreading over the most active points. Thus as the amount of adsorption increases, sites of smaller activity will be gradually covered for which the heat of adsorption may continously decrease.

The second factor for this decrease may be due to the increasing repulsion between the surface and the adsorbate ions. It has been repeatedly noted that the adsorption of the cations from the Crystal Violet have a peptising action on the hydrous oxide so that its surface gets positively charged. It is evident that the adsorption of a cation as that of Crystal Violet will be considerably apposed if the surface of the hydrous oxide is charged positively by the prior adsorption of cations.

It is necessary to offer an explanation for the increase in the heat of adsorption with increasing amount adsorbed so that *Q* and *X/M* curve passes through a maximum. The values of heat of adsorption calculated here are of five hours duration of contact for adsorption and that is when adsorption is not complete. The saturation of adsorption is attained more rapidly at higher temperatures and the adsorption is large leading to greater dissociation of the micelle. It appears that at higher concentrations chemisorption approaches completion with the effect that the negative heat of adsorption increases with increasing amount of adsorption. This is prominently noted for sample A and Sample B, which have more acidic character and therefore adsorb cations more than the other samples of the hydrous oxide.

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A STUDY OF THE INTERACTION BETWEEN ZIRCONIUM NITRATE AND SODIUM SUCCINATE

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[Received on 26th June 1959]

ABSTRACT

The interaction between zirconium nitrate and sodium succinate has been followed by conductometric and electrometric titration methods. It is observed that precipitation occurs when zirconium : succinate ratio is 1:1. The hydrous oxide and the mono succinate of the metal are predominantly formed. By choosing suitable concentrations of the reactants the precipitation of the monosuccinate is easily controlled and the reacting mixtures can be made to give stable and transparent gels. The conductometric and electrometric curves are explained.

In several publications Ghosh and associates[1] have followed the precipitation of various metal silicates adopting electrometric methods. In some of the recent publications from these laboratories the insoluble succinates of iron and aluminium have been investigated by conductometric and electrometric methods[2]. Mehrotra and Kapoor employing similar technique have followed the interaction between zirconyl chloride and sodium mandelate.

When sodium succinate is added to a zirconium nitrate solution, the precipitate first formed, gets quickly dissolved, when the former is in small amount. If the addition of sodium succinate is continued it is noted that there comes a region when a transparent gel is obtained on allowing the interacting solution to stand undisturbed for some time. When however the succinate, zirconium ratio attains the value 1:1 the formation of a permanent white precipitate takes place. The chemical nature of the precipitate has been investigated employing couductometric and electrometric methods.

MATERIALS

Zirconium nitrate employed was of Merck G. R. quality. The zirconium content was estimated by the usual methods[4]. Fresh stock solutions of Merck's extra pure sodium succinate were always employed as it was observed that the solutions could not be stocked for very long periods.

METHOD

Different quantities of sodium succinate were taken in a series of test tubes. In another set of test-tubes were taken fixed quantities of suitable zirconium nitrate solutions. The total volume was kept constant in all the cases. The tubes were

kept in a circulation bath at 28°±0·1°C. The reactants were mixed by adding the solution back and forth for four times. Each mixture was left undisturbed in the circulation bath for an hour after which the conductivity and pH of each was measured.

Conductometric—The apparatus consisted of an L & N. Kohlrausch drum type bridge, length 1000 cm, a tunable headphone, an audiooscillator with a tuning fork giving a constant frequency of 1000 c/sec and an immersion cell of the type G. M. 4221 (Philips & Co.); the set up was operated at 110 V. The measurements were carried out at a bath temperature of 28° ± 0·1°C.

Electrometric—pH measurements were carried out using a Leeds Northrup's pH meter with a glass electrode which gave readings reproducible within 0·05 pH. The measurements were made at a bath temperature 28°±0·1°C.

Gelling time—Gelling time of such mixtures was also determined by the method described by Bose and Mushran[5] and for a comparative study a record for mixtures for which the gelling time was within 5 hours was maintained. The gelling region was thereby determined as indicated in tables I—IV.

The results of the conductometric and electrometric study are compiled in Tables I—IV.

TABLE I

M/5 Ziroconium Nitrate Soln.=8 ml.

Total Vol. 28 ml.

M/5 Sodium succinate (ml.)	pH	Sp. Cond. × 10^3 Ω^{-1}	
0·00	1·80	24·06	(a)
0·20	1·80	25·05	(a)
1·00	1·85	24·33	(a)
2·00	1·90	21·91	(a)
4·00	2·00	17·79	(b)
6·00	2·60	13·91	(b)
8·00	3·80	12·60	(c)
9·00	4·30	13·63	(c)
11·00	4·90	15·34	(c)
13·00	5·25	17·30	(c)
15·00	5·34	18·74	(c)
17·00	5·45	20·80	(c)

(a) no gel (b) transparent gel (c) precipitate.

TABLE II

M/10 Zirconium Nitrate =8 ml.

Total Vol. = 28 ml.

M/10 Sodium succinate (ml.)	pH	Sp. Cond. × 10^3 Ω^{-1}	
0·00	2·00	12·09	(a)
0·20	2·05	12·47	(a)
1·00	2·10	12·24	(a)
2·00	2·18	11·68	(a)
4·00	2·32	9·78	(b)
6·00	2·70	8·64	(b)
8·00	3·90	6·57	(c)
9·00	4·35	7·06	(c)
11·00	4·92	8·02	(c)
13·00	5·25	9·05	(c)
15·00	5·35	10·02	(c)
17·00	5·50	11·53	(c)

(a) no gel (b) transparent gel (c) precipitate

TABLE III

M/20 Zirconium Nitrate = 8 ml.

Total Vol. = 28 ml.

M/20 Sodium succinate (ml.)	pH	Sp. Cond. × 10^3 Ω^{-1}	
0·00	2·32	6·94	(a)
0·20	2·33	7·10	(a)
1·00	2·35	7·03	(a)
2·00	2·38	6·81	(a)
4·00	2·45	5·77	(b)
6·00	2·75	4·38	(b)
8·00	3·70	3·69	(c)
9·00	4·20	3·90	(c)
11·00	4·65	4·34	(c)
13·00	5·10	5·06	(c)
15·00	5·25	5·59	(c)
17·00	5·55	6·26	(c)

(a) no gel (b) transparent gel (c) precipitate

TABLE IV

M/40 Zirconium Nitrate=8 ml.

Total Vol. = 28 ml.

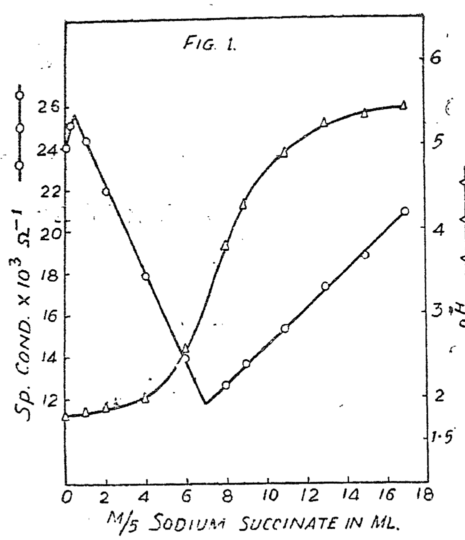
M/40 Sodium succinate (ml).	pH	Sp. Cond. × 10^3 Ω^{-1}	
0·00	2·58	3·05	(a)
0·20	2·58	3·82	
1·00	2·52	3·80	
2·00	2·65	3·62	
4·00	2·80	3·02	(b)
6·00	3·10	2·31	
8·00	3·90	1·92	(c)
9·00	4·25	2·02	
11·00	4·80	2·10	
13·00	5·10	2·59	
15·00	5·30	2·93	
17·00	5·40	3·24	

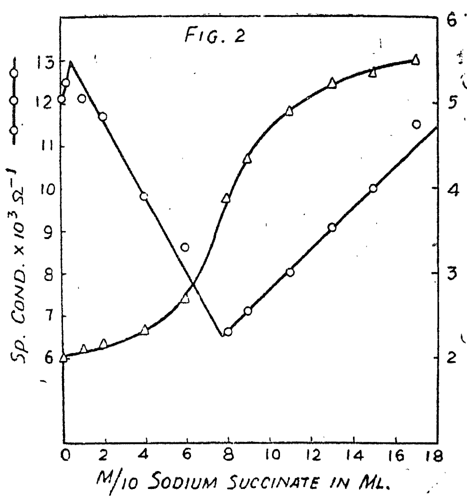
(*a*) no gel (*b*) transparent gel (*c*) precipitate

These results are represented graphically in Figs. 1—4.

DISCUSSION

A perusal of Figs. 1—4 shows that the stepwise addition of increasing quantities of sodium succinate solutions to a fixed quantity of zirconium nitrate solution produces a slight increase in the conductivity in the initial stages. This is followed by a drop until the molar zirconium, succinate ratio becomes 1:1. Here a break occurs and the conductance subsequently increases.





A solution of zirconium nitrate is acidic due to the hydrolysis of the salt as:

$$Zr\,(NO_3)_4 + H_2O \rightleftharpoons HNO_3 + Zr\,(NO_3)_3\,OH$$

$$Zr\,(NO_3)_3\,OH + H_2O \rightleftharpoons HNO_3 + Zr\,(NO_3)_2\,(OH)_2$$

$$Zr\,(NO_3)_2\,(OH)_2 + H_2O \rightleftharpoons HNO_3 + Zr\,(NO_3)\,(OH)_3$$

$$Zr\,(NO_3)\,(OH)_3 + H_2O \rightleftharpoons HNO_3 + Zr\,(OH)_4.$$

A solution of sodium succinate is however slightly alkaline as:

$$Na_2\,C_4H_4O_4 + H_2O \rightleftharpoons NaHC_4H_4O_4 + NaOH$$

The titration of zirconium nitrate against a weak base sodium succinate would therefore bring about a gradual increase of pH because of the removal of the hydronium ions by the formation of water as:

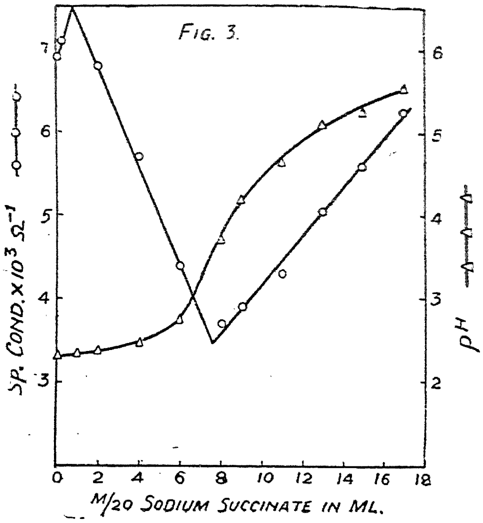
$$H^+ + OH^- \rightleftharpoons H_2O$$

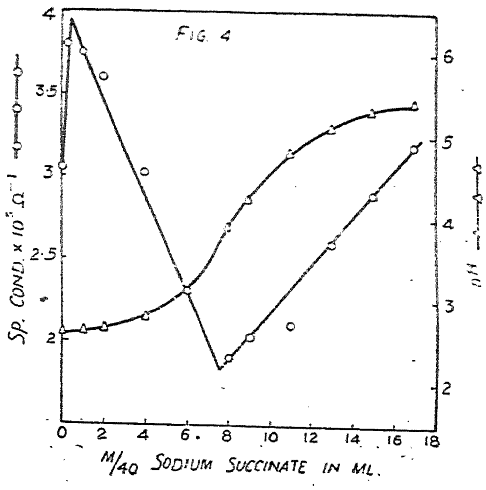
This scheme of reaction suggests a fall in electrical conductance because of the initial removal of the highly conducting hydronium ions. The experimental data, however, differ from the expected result and a rise in conductivity is perceivable in the earlier stages. It must be remembered that the removal of the hydronium ions is also a companied by the rapid replacement of the zirconium ions by the more conducting sodium ions. It is evident therefore that the latter effect predominates the former and an initial rise in conductivity is observed.

On the further addition of sodium succinate the conductivity falls rapidly and continues falling until the zirconium, succinate ratio is 1:1. This is clearly understood. An inspection of Figs. 1—4 on the measurements of the hydrogen ion concentrations shows that in the earlier stage there is a very slight decrease in pH but as more and more of the succinate is added the decrease is more rapid, an inflexion in the pH curve occurring when the zirconium, succinate ratio is 1:1. Undoubtedly, therefore, the hydronium ions, one of the important contributors in

the electrical conductance decrease rapidly as the zirconium, succinate ratio approaches the value 1:1. Further, a decrease in the hydronium ions is also expected by their removal due to adsorption by the precipitate of the mono-succinate which appears according to:

$$Zr\,(OH)_3\,(NO_3) + NaHC_4H_4O_4 \rightleftharpoons Zr\,(OH)_3\,(HC_4H_4O_4) + NaNO_3$$





It is evident therefore that though in the initial stages the precipitate is likely to contain the hydrous oxide but at later stages with the gradual addition of larger quantities of the succinate the precipitate is mainly of zirconium mono-succinate.

It is interesting to note, that the gelation of the interacting mixtures starts in the region where the conductivity decreases after the initial increase *i. e.* in the region where larger proportion of the zirconium mono succinate is present (Tables I—IV). A necessary condition of gel formation is therefore a larger proportion of the zirconium mono-succinate.

ACKNOWLEDGEMENTS

Thanks of the authors are due to Prof. S. Ghosh, D.Sc., F.R.I.C., F.N.I. for kind interest during these investigations and to the U. P. Scientific Research Committee for the award of a scholarship to one of us (Y. D. U.).

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ADSORPTION OF CRYSTAL VIOLET ON HYDROUS CHROMIUM OXIDE

PART III. RATE OF ADSORPTION, ENERGY OF ACTIVATION AND MECHANISM OF ADSORPTION

By

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[Received on 4th May, 1959]

ABSTRACT

The adsorption of Crystal Violet has a rate which increases with increasing time of contact and also of temperature. The energy of activation, E, for adsorption has been calculated by comparing the rates at two temperatures. The results show that

1. The adsorption of Crystal Violet is a slow process and tends towards unimolecularity at high concentrations where complete saturation takes place. However, at lower initial concentrations of the dye, the kinetics of adsorption seems to be of zero order.

2. The energy of activation for the samples are positive and are not high as compared to chemical reactions in solution taking place at ordinary temperature.

3. Generally, the heat of activation for adsorption increases with increasing coverage of the surface.

4. The adsorption of Crystal Violet is a case of activated adsorption or better chemisorption preceeded by physical adsorption in earlier stages.

5. Hydrous chromium oxide is amphotine in nature and it is probable that acidic nature of hydrous oxide initiates the chemisorption of the coloured cation of Crystal Violet.

6. The whole process of adsorption of dye include dissociation of aggregated micelle, followed by primary adsorption and subsequent chemical union of the basic group with the acid group CrO_2 constituting the surface of the hydrous oxide.

As both the process (*b*) and (*c*) occur simultaneously no stoichiometric relation exists and taking up of Crystal Violet may be described as the formation of adsorption complex.

In the first and second parts of this series[1-2], it has been shown that the adsorption of Crystal Violet dye by hydrous chromium oxide increases with increasing concentration of the dye, time and temperature. In this paper the rate of adsorption from solutions by different samples of hydrous oxide at different temperatures is discussed and the heat of activation for the adsorption has been calculated. It has been concluded that with increasing coverage, which may be taken as proportional to the amount of adsorption, the heat of activation gradually increases.

As already reported, the adsorption of Crystal Violet by hydrous chromium oxide is a slow process, the amount adsorbed increasing with time. It takes about 96 to 120 hours for attaining complete saturation. Similar results have been reported in the case of adsorption of oxygen on cobalt chromite catalyst[3], hydrogen on zinc oxide catalyst[4], adsorption of ammonia, H_2, C_2H_4, CO_2, NO, CH_4, O_2, N_2, He and Ne on chabasite[5]. The adsorption of such dye stuffs[6] as Duranol Blue G 300 and Dispersel Fast Red R 150 also increases with increase of time on nylon. The Figs. 1, 2 and 3 describe the amount of adsorption recorded by us for different initial concentrations of Crystal Violet with time. The curves show that their concavity in the initial stage towards time axis diminishes with the decrease of initial concentration of Crystal Violet taken for the adsorption. It tends to become linear for dilute dye solutions.

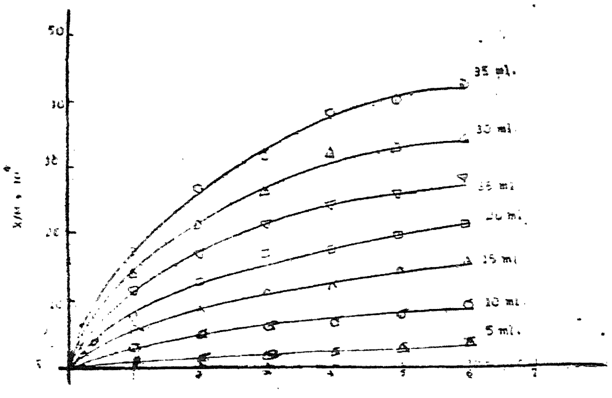


Fig. 1. Rate of adsorption at 40°C for Hydrous chromium oxide sample A.

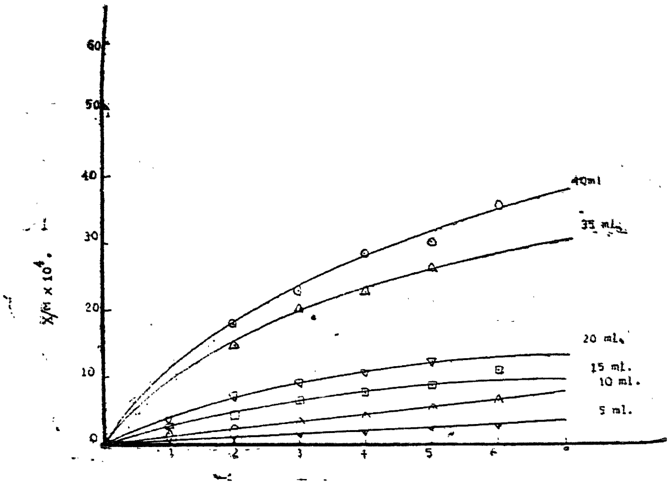


Fig. 2. Rate of adsorption at 30° C. for hydrous chromium oxide sample B.

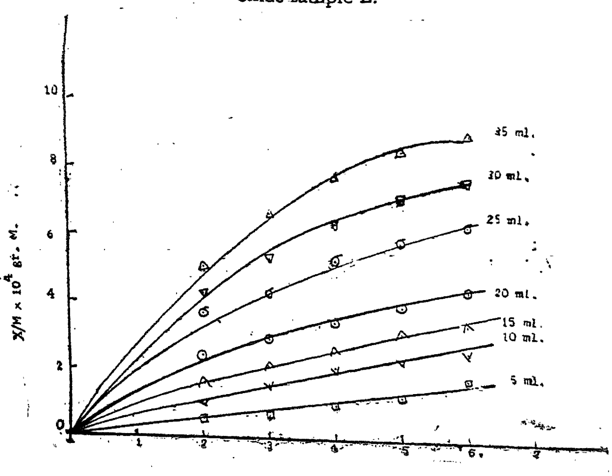


Fig. 3. Rate of adsorption at 30°C for hydrous chromium oxide sample C.

It is generally believed[7] that the physical adsorption is as rapid and equal to the time taken by the molecule to reach the surface. The slow rate of adsorption may, therefore, be either due to chemisorption, chemical reaction, solution or to the inability of the molecule to get in contact with the surface of the adsorbent. The rate of the amount of dye adsorbed, which is given by the curvature of the curves indicates that it is fairly fast in early stage. The early adsorption, therefore, may be physical in nature, but with the increase of time, the rate of adsorption becomes slow which suggests chemisorption. Taylor[8] has pointed out that the rate of chemisorption increases exponentially with temperatue as for a chemical reaction. In the present case the rate of adsorption is found to increase enormously with rise in temperature.

We have, however, found that none of the simple equations of chemical kinetics, for example, those for zero, uni, bimolecular order etc. are not applicable. Langmuir's[9] equation on the rate of adsorption on the free surface is as follows :

$$\ln \frac{V_c}{V_c - V} = k.\ t.$$

where V and V_c are the volume of gas adsorbed after time t and at equilibrium respectively. The above reaction is also not applicable to the experimental results obtained here. However, from the nature of the curves, the rate of lower initial concentrations of the dye, it appears to be of zero order, but at higher concentrations of the dye it tends towards unimolecularity.

The rate of adsorption for the samples of hydrous oxides A and B is considerably effected by temperature. Energies of activation have been calculated from the temperature co-efficient of the rate. For chemical changes the heat of activation is given by

$$-\frac{E}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) = \ln K_{T_1} - \ln K_{T_2}$$

on calculating V_{T_1} and V_{T_2} at tempratures T_1 and T_2 respectively from the reaction velocity, E can be calculated.

In order to calculate E it is necessary to know the value of K_{T_1} and K_{T_2}. Now the rate of adsorption as will be seen from the experimental curves, is related with the concentration of the adsorbate, so that

$$-\left(\frac{dc}{dt}\right)_{T_1} = K_{T_1} \cdot f(C_1) \quad \dots \quad (1)$$

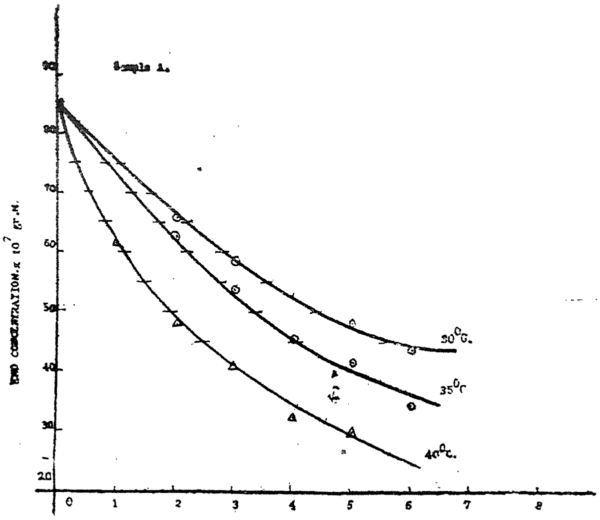
where C_1 denotes the concentration of the dye at any instant. Again at highe temperatures T_2 we have

$$-\left(\frac{dc}{dt}\right)_{T_2} = K_{T_2} \cdot f(C_2) \quad \dots \quad (2)$$

the value of $f(C)$ is not exactly known and therefore the value of the specific rate constants cannot be calculated. We may, however, find out the rate of adsorption at two temperatures T_1 and T_2 for the same range of the end concentration of the dye and for the same original concentration of the dye.

Thus
$$\frac{\left(\frac{dc}{dt}\right)_{T_1}}{\left(\frac{dc}{dt}\right)_{T_2}} = \frac{K_{T_1}}{K_{T_2}}$$

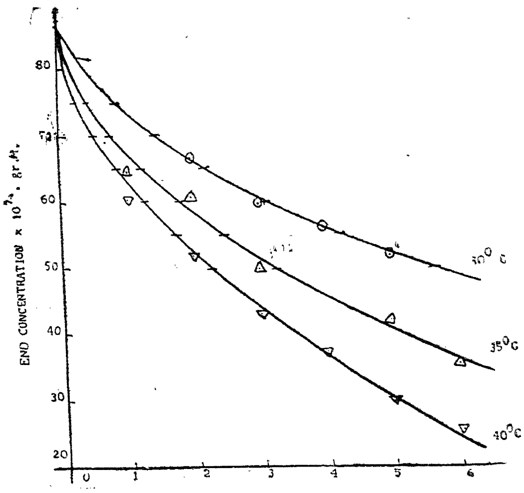
The values of $\left(\frac{dc}{dt}\right)_{T_1}$ and $\left(\frac{dc}{dt}\right)_{T_2}$ for the same concentration of the dye, can be calculated from the graph between end concentration at different temperatures by extrapolating the time dt for the same difference of concentrations at temperatures T_1 and T_2. The ratio of values $\left(\frac{dc}{dt}\right)_{T_1}$ and $\left(\frac{dc}{dt}\right)_{T_2}$ gives the ratio of K_{T_1} and K_{T_2}.



Time in Hours.

Fig. 4. Plotted curve between residual end concentration of the dye at different time intervals for extrapolating the values of energy of activation for hydrous chromium oxide sample A.

Sample B .



Time in Hours.

Fig. 5. Plotted curve between residual end concentration of the dye at different time intervals for extrapolating the values of energy of activation for hydrous chromium oxide sample B.

In tables given below, energies of activation has been calculated by extrapolating the values of K_{T_1} and K_{T_2} from the Figs. 4 and 5 drawn between end concentration left over after adsorption, and the time and taking R = 1·987 calories, degrees^{-1} mole^{-1}

TABLE 1

Sample A.

End conc. between	$\log\left(\frac{dc}{dt}\right)$ 30°C	$\log\left(\frac{dc}{dt}\right)$ 35°C	$\log\left(\frac{dc}{dt}\right)$ 40°C
70-65	—9·5977	—9·4857	—9·2966
60-55	—9·7024	—9·5775	—9·4014
55-50	—9·7738	—9·6170	—
50-45	—9·9365	—9·7024	– 5·5977

TABLE 2

Sample A. Energy of Activation.

End. conc. between	E (30°-35°)	E (30°-40°)	Mean E
70-65	9566·0	13067·3	11318·6
60-55	10667·8	13067·0	11865·4
55-50	13392·4	—	13392·4
50-45	19994·7	14703·5	17349·1

TABLE 3

Sample B.

End. conc. between	$\log\left(\frac{dc}{dt}\right)$ 30°C	$\log\left(\frac{dc}{dt}\right)$ 35°C	$\log\left(\frac{dc}{dt}\right)$ 40°C
75-70	—9·6355	—9·4313	—9·2966
65-60	—9·8115	—9·5977	—9·4594
60-55	—9·9085	—9·6702	—9·5340
55-50	—9·9956	—9·7466	—9·5775

TABLE 4

Sample B

Energy of activation

End conc. between	E (30°-35°)	E (35°-40°)	E (30°-40°)	Mean E
75-70	17440·9	11884·5	14707·8	14677·4
65-60	18602·5	12202·2	15280·7	15361·8
60-55	20353·4	12016·9	16252·8	16207·7
55-50	21267·3	14919·7	13145·0	18110·6

The results of energies of activation for different samples are positive and its magnitude is specially low at smaller coverage of the surface, when compared to chemical reactions in soultions taking place at ordinary tmeperatures. It is further seen that with increasing coverage or greater time of contact, the amount of adsorption, the heat of activation has a tendency to increase. This clearly shows that the most active spots on the surface are filled up first by the adsorbate molecules or ions for which the heat of activation for adsorption is necessarily small.

Chemisorption, in many instances, has been known to be instantanous. Taylor and Williamson[10], however, found that the rate of adsorption of hydrogen on manganous oxide catalyst is measurable even at 305°C and similar cases of slow adsorption have been already cited. Taylor[7] calculated the energy of activation for an adsorption process and various workers are of the opinion that energies of activation calculated from adsorption rate measurements are due to other factors *viz.*, solution, diffusion, migration or reaction in the surface rather than the chemisorption process itself. If we, however, assume that the adsorbent has unsaturated valence force and the chemisroption process has some similarity to a chemical reaction, such an adsorption will require energy of activation although its magnitude may be very small.[11]

The adsorption of Crystal Violet, therefore, is a typical case of activated adsorption preceeded by physical adsorption in eariler stages which may, however, be instantaneous. Since we know that on the surface active spots are statistically distributed for adsorption it is but natural that more active spots will be covered first. Thus the heat of activation will be less in the earlier stages.

MECHANISM AND CONCLUSION

Form the results presented in this series of papers, we may conclude that the taking up of Crystal Violet by hydrous chromium oxide is mainly of chemical nature or chemisorption, which is however, preceeded by physical adsorption. Hydrous oxide forms lakes with dyes. For a long time such lakes were believed to be definite chemical compunds formed with the dye and the oxide. Blitz[12] however, suggested that lakes might not be definite chemical compounds and Weiser[13] is of the opinion that certain lakes may be definite compounds though it is more probable that most lakes are adsorption complexes formed with the mordant and the dye.

The composition of such lakes varies with the condition of formation. All adsorption experiments for Crystal Violet with different samples of hydrous oxide reported by us show that it varies with the concentration of dye, time, temperature and the nature of adsortion curves indicate the absence of the formation of any chemical compound. Similar results have been obtained by Ackerman[14] for the coloured lakes formed from triphenylmethane dye, acid green and the acid dye, azogeranine with the hydrous oxide of aluminium, zinc and tin.

Hydrous chromium oxide is amphoteric in character as has been pointed out earlier and it can be represented as

$$Cr(OH)_3 \rightleftharpoons Cr(OH)^+_2 + (OH)^- \quad \ldots (1)$$

$$Cr(OH)^+_2 \rightleftharpoons CrO(OH) + H^+ \quad \ldots (2)$$

$$CrO(OH) \rightleftharpoons CrO_2^- + H^+ \quad \ldots (3)$$

The above change show that chromium hydrous oxide has both acidic and basic nature. Equation (2) and (3) describe the acidic nature and (1) shows its basic nature. It is probable that the existence of CrO^-_2 group on solid hydrous oxide initiates the chemisorption of the coloured cation of Crystal Violet.

Crystal Violet micelles, ordinarily yield an aggregated cation similar to colloidal electrolytes. The aggregated cation dissociates to less aggregated ones either on dilution or on increasing temperature. The chemisorption occurs because of basic tertiary group in the cation which, it appears, become more available from less aggregated colloidal micelle.

It has been shown in this paper that there exists a heat of activation for the taking up of the coloured cation of Crystal Violet for the samples A and B of hydrous chromium oxide, though primary process of adsorption is believed not to require any energy of activation. The adsorbed molecules after primary adsorption diffuse into the solid or they may combine with some other atoms or groups, which process may require activation energy. In the present case it is probable that adsorption occurs due to the presence of tertiary basic group in the dye cation and the active acid groups present in the hydrous oxide. Moreover, there is an equilibrium between the aggregated and simple cations of the dye in solutions and greater adsorption of simpler cations will lead to the greater dissociation of the aggregated units. The whole process of adsorption of the dye by the hydrous oxide will therefore include (*i*) dissociation of aggregated cation (*ii*) primary adsorption and (*iii*) subsequent chemical union of the basic groups with the acidic group CrO^-_2 constituting the surface of the hydrous oxide. As the amount of dye taken up by the solid hydrous oxide is due to both the factors (*ii*) and (*iii*), existence of no definite compound could be observed. It has been found in a previous paper of the series that it is endothermal in nature in the earlier stages of adsorption. This is due to process (*i*).

We are, therefore, of the opinion that lake formation is intimately related with the reactive groups present in the dye and the solid. We have further shown that hydrous oxide of chromium, which is ordinarily considered to be basic mordant, can be conveniently made to adsorb large amounts of a basic dye provided its acidic character can be evoked especially by precipitating it with a little excess of an alkali.

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DIFFUSION OF ANIONIC METAL TARTRATE COMPLEXES THROUGH FILTER PAPER

PART II. AQUEOUS METHANOL AS SOLVENT

By

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[Received on 11th May, 1959]

ABSTRACT

Attempts to separate Cu^{++}, Ni^{++}, Co^{++}, Cd^{++}, and Fe^{+++} in mixtures, by filter paper strip chromatography have been made, using tartrate as complexing agent and aqueous methanol as solvent. The effect of adding varying concentrations of the complexing agent in the solution has been studied. The R_M, R_L and R_T values have been determined and recorded.

In general, good separation of ions occurs when total metal to tartrate ratio is below 1 : 1, and with higher concentrations of tartrate separation is not possible.

In a number of previous publications, we have reported our study on the diffusion of metal ions through filter paper strips in the presence of varying concentrations of complexing agents. We have thus studied the behaviour of various metal ammines (1), anionic oxalate (2, 3), tartrate (4), and citrate (5) complexes of Cu^{++}, Ni^{++}, Co^{++}, Fe^{++}, Fe^{+++} and Cd^{++} and have noted the effect of variation of concentration of the complexing agent on the R_F values. The solvent employed by us was aqueous ethanol. In other communications (6, 7) we have recorded our attempts in the separation of metal ions in the presence of tartrate using the same solvent.

In this paper we have extended the studies to separations using aqueous methanol as solvent. Varying concentrations of methanol have been tried and only those giving satisfactory results have been recorded. The paper describes some of the typical observations out of a large number of experiments.

EXPERIMENTAL

Standard solutions of sodium tartrate, cupric sulphate, cobalt sulphate, nickel sulphate, ferric sulphate and cadmium chloride were prepared using reagent grade chemicals. The method adopted was the strip filter paper chromatographic method, using an arrangement described by Gage, Douglass and Wender (8). Various concentrations of methanol were tried and it was found that 50% methanol was suitable as a solvent in all the cases except in Table I where 100% methanol gave better separation. A series of mixtures containing equal concentrations of metal solutions with varying proportions of sodium tartrate were prepared, keeping the total volume constant. Column 2 of the tables show the ratio of the total concentration of the metals (obtained by adding the concentrations in molarity of the metals) to the concentration of tartrate added. The mixtures were spotted on filter paper strips prepared from Whatman filter paper No. 1. The chromatograms were run at constant temperature in a room, with temperature controlled at 30°C and the time allowed was 1·5 hours for diffusion. R_F, R_M, R_L and R_T values were determined as described by us earlier[6].

TABLE I

Final concentration of each of the metal ions = 0·05 M

(A mixture of H_2S water and dimethylglyoxime used for developing)

No.	Ratio Total metal : $Tart^{2-}$	Values of Cadmium (II) $-R_M$	R_L	R_T	Values of Nickel (II) $-R_M$	R_L	R_T
1	1 : 0	0·00	0·50	0·49	– 0·01	0·49	0·00
2	1 : 0·1	—0·01	0·49	0·48	—0·03	0·48	0·00
3	1 : 0·2	—0·01	0·49	0·42	—0·19	0·42	0·00
4	1 : 0·3	—0·01	0·49	0·42	—0·19	0·42	0·00
5	1 : 0·4	—0·15	0·46	0·35	—0·33	0·35	0 00
6	1 : 0·5	—0·17	0·45	0·27	—0·48	0·27	0·00
7	1 : 0·6	– 0·17	0·45	0 25	—0·55	0·25	0·00
8	1 : 0·7	– 0·17	0·44	0·24	—0·60	0·24	0·00
9	1 : 0·8	—0·19	0·43	0·23	—0·63	0·23	0·00
10	1 : 0·9	No movement			—0·65	0·20	0·00
11	1 : 1·0	No movement			—0·65	0·20	0·00

In this case 100% methanol was used for the separation. The separation of nickel (II) and cadmium (II) ions is possible up to one equivalent of tartrate added. With higher concentrations of the complexing agent both the ions do not move at all. However, when the ratio of metal : concentration of tartrate is 1 :0·9 to 1 : 1, only nickel (II) ion moves on the chromatograms, while cadmium (II) ions do not move at all. A good separation is obtained with the addition of 0·4 to 0·7 equivalents of complexing agent. It may be noted from Table I that R_L and R_M values of Cd^{++} and Ni^{++} decrease with small additions of tartrate and continue to decrease by increasing the concentration of the complexing agent. R_T value of Ni^{++} is zero in all cases.

TABLE II

Final concentration of each of the metal ions = 0·05 M

(A mixture of H_2S water and $K_4Fe(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0·55	0·81	0·69	0·29	0·69	0·00
2	1 : 0·1	0·55	0·81	0·67	0·25	0·67	0·00
3	1 : 0·2	0·52	0·81	0·59	0·10	0·59	0·00
4	1 : 0·3	0·48	0·81	0·49	−0·07	0·49	0·00
5	1 : 0·4	0·48	0·81	0·61	−0·10	0·47	0·00
6	1 : 0·5	0·48	0·80	0·60	−0·07	0·49	0·14
7	1 : 0·6	0·45	0·79	0·67	0·25	0·67	0·37
8	1 : 0·7	0·45	0·79	0·68	0·27	0·68	0·54
9	1 : 0·8	0·41	0·76	0·69	0·29	0·69	0·61
10	1 : 0·9	0·41	0·76	0·71	0·33	0·71	0·61
11	1 : 1	0·41	0·76	0·72	0·35	0·72	0·61
12	1 : 1·3	0·39	0·75	0·72	0·35	0·72	0·62

The separation of Co^{++} and Cu^{++} ions is effected upto 1·3 equivalents of tartrate added. With higher concentrations of the complexing agent the separation is not possible. It may be seen that a good separation is obtained when 0·2 to 0·7 equivalents of complexing agent are used. From Table II it may be seen that the R_L and R_M values of Co^{++} do not change in the beginning with the addition of the complexing agent, but later begin to decrease with the increase in the concentration of the complexing agent and finally becomes constant. The R_L and R_M values of Cu^{++} decrease with the additions of the complexing agent and continue to decrease on increasing the concentration of the same, finally to increase and then become constant. The R_T value of Cu^{++} is zero upto 0·4 equivalents of the complexing agent.

TABLE III

Final concentration of each of the metal ions = 0·05 M

(A mixture of K_4 Fe $(CN)_6$ and dimethyl glyoxime used for developing.)

No.	Ratio Total : $Tart^{2-}$ metal	Values of Nickel (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0·63	0.85	0·73	0·37	0·73	0·00
2	1 : 0·1	0·60	0·84	0·69	0·29	0·69	0·00
3	1 : 0·2	0·60	0·84	0·69	0·29	0·69	0·00
4	1 : 0·3	0·60	0·84	0·70	0·31	0·70	0·00
5	1 : 0·4	0·57	0·83	0·72	0·35	0·72	0·00
6	1 : 0·5	0·57	0·83	0·72	0·35	0·72	0·51
7	1 : 0·6	0·55	0·82	0·73	0·37	0·73	0·60
8	1 : 0·7	0·55	0·82	0·74	0·39	0·74	0·60
9	1 : 0·8	0·50	0·80	0·74	0·39	0·74	0·60
10	1 : 0·9	0·43	0·77	0 74	0·39	0·74	0·60

It may be seen that separation of the ions is obtained upto 0·9 equivalents of the complexing agent used. Beyond 0·9 equivalents of the same, separation is not possible, due to the spreading and overlapping of the zones. R_T value of Cu^{++} is zero up to the addition of 0·4 equivalents of the complexing agent. As the concentration of the same is increased the R_T value increases and finally becomes constant. The R_L and R_M values of Cu^{++} behave in a similar manner as recorded in previou tables. It may be seen from Table III that the R_L and R_M values of Ni^{++} decrease with the small additions of the complexing agent and continue to decrease as the concentration of the complexing agent increases.

TABLE IV

Final concentration of each of the metal ions = 0·05 M

(A mixture of H_2S water and $K_4\,Fe\,(CN)_6$ used for developing)

No.	Ratio Total : Tart^{2-} metal	Values of Cadmium (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	0·57	0·81	0·76	0·43	0·76	0·00
2	1 : 0·1	0·57	0·81	0·72	0·37	0·72	0·00
3	1 : 0·2	0·55	0·81	0·64	0·17	0·63	0·00
4	1 : 0·3	0·55	0·81	0·69	0·27	0·68	0·00
5	1 : 0·4	0·52	0·79	0·69	0·27	0·68	0·00
6	1 : 0·5	0·52	0·79	0·63	0·27	0·68	0·00
7	1 : 0·6	0·52	0·79	0·70	0·31	0·70	0·49
8	1 : 0·7	0·50	0·78	0·75	0·41	0·75	0·56
9	1 : 0·8	0·48	0·77	0·75	0·41	0·75	0·59

The separation of Cd^{++} and Cu^{++} ions is possible upto 0·8 equivalents of complexing agent added. It may be seen that a good separation of the ions from the supernatent liquid occurs when 0·2 to 0·4 equivalents of the complexing agent are used, though a part remains settled as a precipitate. It may be noted from table IV that the R_L and R_M values of Cd^{++} do not change with small additions of the complexing agent. As the concentration of the same is increased the value decrease.

The R_L and R_M values of Cu^{++} behave in a similar manner as recorded previously.

TABLE V

Final concentration of each of the metal ions = 0·05 M

(H_2S water used for developing)

No.	Ratio Total : Tartrate metal	Values of Cobalt (II)			Values of Cadmium (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0·9	0·55	0·81	0·40	−0·21	0·40	0·00
2	1 : 1·0	0·52	0·80	0·59	−0·27	0·37	0·00
3	1 : 1·3	0·52	0·80	0·62	−0·33	0·32	0·00
4	1 : 1·5	0·52	0·80	0·62	−0·39	0·31	0·00
5	1 : 1·7	0·52	0·80	0·62	−0·41	0·31	0·00
6	1 : 2·0	0·52	0·80	0·62	−0·41	0·31	0·00
7	1 : 2·5	0·52	0·80	0·62	−0·41	0·31	0·00
8	1 : 3·0	0·52	0·80	0·62	−0·41	0·31	0·00
9	1 : 4·0	0·50	0·79	0·62	−0·41	0·31	0·00

From 0·2 to 0·8 equivalents of tartrate added it is difficult to note the R_L and R_T values of Cd^{++} and Co^{++} due to the spreading and overlapping of the zones and no separation is possible and hence the results have not been shown. The separation of Co^{++} and Cd^{++} ions is effected when 0·9 or more equivalents of the complexing agent are added. With the addition of one or more equivalents of the complexing agent, the R_L and R_M values of Co^{++} become constant. It may be seen from Table V that the R_L and R_M values of Cd^{++} decrease with the increase in the concentration of tartrate and finally become constant. R_T value of Cd^{++} is zero in all the cases.

TABLE VI

Final concentration of each of the metal ions = 0·05 M

($K_4Fe(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Copper (II) $-R_M$	R_L	R_T	Values of Iron (III) $-R_M$	R_L	R_T
1	1 : 0	0·82	0·88	0·85	0·60	0·85	0·00
2	1 : 0·1	0·75	0·86	0·84	0·57	0·84	0·00
3	1 : 0·2	0·75	0·86	0·84	0·57	0·84	0·00
4	1 : 0·3	0·75	0·86	0·83	0·55	0·83	0·22
5	1 : 0·4	0·72	0·85	0·81	0·52	0·81	0·41
6	1 : 0·5	0·68	0·84	0·81	0·52	0·81	0·67
7	1 : 0·6	0·68	0·84	0·81	0·52	0·81	0·70
8	1 : 0·7	0·68	0·84	0·80	0·50	0·80	0·70
9	1 : 0·8	0·68	0·84	0·80	0·50	0·80	0·70
10	1 : 0·9	0·65	0·83	0·80	0·48	0·80	0·70
11	1 : 1·0	0·65	0·83	0 80	0·48	0·80	0·70
12	1 : 1·3	0·65	0·83	0·80	0·48	0·80	0 70

The separation of Fe^{+++} and Cu^{++} ions is possible up to 1·3 equivalents of tartrate added. With higher concentrations of the same, separation is not possible under the experimental conditions. It may be noted from the observations recorded in Table VI that the R_L and R_M values of Cu^{++} and Fe^{+++} decrease constantly with the increase in the concentration of tartrate and finally become constant. The R_T value of Cu^{++} and Fe^{+++} becomes constant by adding 0·7 or more equivalents of the complexing agent.

TABLE VII

Final concentration of each of the metal ions = 0·05 M

(A mixture of dimethyl glyoxime and $K_4 Fe(CN)_6$ used for developing)

No.	Raito Total metal : $Tart^{2-}$	Values of Nickel (II) $-R_M$	R_L	R_T	Values of Iron (III) $-R_M$	R_L	R_T
1	1 : 0	0·82	0·90	0·86	0·63	0·86	0·00
2	1 : 0·1	0·82	0·90	0·86	0·63	0·86	0·00
3	1 : 0·2	0·82	0·90	0·86	0·63	0·86	0·00
4	1 : 0·3	0 82	0·90	0·85	0·60	0·85	0·20
5	1 : 0·4	0·82	0·90	0·84	0·57	0·84	0·34
6	1 : 0·5	0·82	0·90	0·84	0·57	0·84	0·45
7	1 : 0·6	0·82	0·90	0·83	0·55	0·83	0·52
8	1 : 0·7	0·82	0·90	0·83	0·55	0·83	0·58
9	1 : 0·8	0·82	0·90	0·82	0·52	0·82	0·58
10	1 : 0·9	0·82	0·90	0·82	0·52	0·82	0·58
11	1 : 1·0	0·82	0·90	0·82	0·52	0·82	0·59
12	1 : 1·3	0·72	0·88	0·82	0·52	0·82	0·59
13	1 : 1·5	0·68	0 87	0·82	0·50	0·82	0·59
14	1 : 1·7	0·68	0·87	0·82	0·52	0·82	0·59
15	1 : 2·0	0·68	0·87	0·82	0·52	0·82	0·59
16	1 : 2·5	0·68	0·87	0·82	0·52	0·82	0·59

The separation of Ni^{++} and Fe^{+++} ions is possible up to the addition of 2·5 equivalents of tartrate. With higher concentration of the same, separation is not possible. A good separation is obtained with the addition of 0·4 to 0·9 equivalents of tartrate. The R_L and R_M values of Ni^{++} and Fe^{+++} do not initially change with addition of tartrate but decrease with very high concentrations of the complexing agent. Finally they become constant. The R_T value of Fe^{+++} increases with increasing of the concentration of the complexing agent and finally it becomes constant with one equivalent of the same.

TABLE VIII

Final concentration of each of the metal ions $=0{\cdot}05$ M

(A mixture of H_2S water and $K_4Fe(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II) $-R_M$	R_L	R_T	Values of Iron (III) $-R_M$	R_L	R_T
1	1 : 0	0·86	0·91	0·86	0·63	0·86	0·00
2	1 : 0·1	0·86	0·91	0·85	0·60	0·85	0·00
3	1 : 0·2	0·86	0·91	0·82	0·52	0·82	0·00
4	1 : 0·3	0·86	0·91	0·82	0·52	0·82	0·21
5	1 : 0·4	0·86	0·91	0·82	0·52	0·82	0·36
6	1 : 0·5	0·86	0·91	0·82	0·52	0·82	0·42
7	1 : 0·6	0·82	0·90	0·81	0·50	0·81	0·59
8	1 : 0·7	0·82	0·90	0·81	0·50	0·81	0·62
9	1 : 0·8	0·82	0·90	0·81	0·50	0·81	0·62
10	1 : 0·9	0·82	0·90	0·81	0·50	0·81	0·62
11	1 : 1·0	0·82	0·90	0·80	0·48	0·80	0·62
12	1 : 1·3	0·82	0·90	0·80	0·48	0·80	0·62

The separation of Co^{++} and Fe^{+++} ions is possible upto the addition of 1·3 equivalents of tartrate. With higher concentrations of tartrate the separations occur in a diffuse state. When more than 1·5 equivalents of tartrate are added separation is not possible and hence the results have not been recorded. From Table VIII it may be noted that the R_L and R_M values of Co^{++} behave in a similar manner as in Table II. The R_L and R_M values of Fe^{+++} behave in a similar manner as in Table VI. The R_T value of Fe^{+++} becomes constant with higher concentrations of complexing agent.

TABLE IX

Final concentration of each of the metal ions=0·042 M

(A mixture of H_2S water and $K_4Fe(CN)_6$ used for developing).

No.	Total metal : Ratio $Tart^{2-}$	Values of Cadmium (II)			Values of Copper (II)			Values of Iron (III)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0·234	1·00	0·91	0·90	0·86	0·90	0·86	0·65	0·86	0·21
2	1 : 0·313	1·00	0·91	0·90	0·86	0·90	0·85	0·63	0·85	0·35
3	1 : 0·39	1·00	0·91	0·90	0·86	0·90	0·83	0·57	0·83	0·41
4	1 : 0·47	1·00	0·91	0·88	0·78	0·88	0·81	0·52	0·81	0·59
5	1 : 0·53	1·00	0·91	0·88	0·78	0·88	0·82	0·55	0·82	0·66
6	1 : 0·60	1·00	0·91	0·88	0·78	0·88	0·82	0·55	0·82	0·66

The separation of Cd^{++}, Cu^{++} and Fe^{+++} ions is possible when 0·234 to 0·60 equivalents of tartrate are used. When the ratio of metal : concentration of tartrate is 1:0·7 to 1:0·9 the Fe^{+++} ions are found to diffuse into these of Copper (II). With a ratio 1:1 to 1:1·6 there is only a separation of the Cd^{++} ions and with higher concentrations of the same separation is not possible. Hence the results beyond 0·60 equivalents of the complexing agent have not been shown. It may be noted from the observations recorded in Table IX that the R_L and R values of Cd^{++} do not change with the additions of tartrate. The R_L and R values of Cu^{++} do not change with the small additions of tartrate but gradually decrease with higher concentrations of the same. The R and R_M values of Fe^{+++} initially decrease with the additions of tartrate but afterwards they increase and finally become constant. The R_T value of Fe^{+++} becomes constant with higher concentration of the complexing agent.

TABLE X

Final concentration of each of the metal ions = 0·042 M

(A mixture of dimethyl glyoxime and K_4 Fe $(CN)_6$ used for developing)

No.	Ratio Total metal : $Tart^{2-}$	Values of Nickel (II)			Value of Copper (II)			Values of Iron (III)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	1·06	0·93	0·91	0·95	0·91	0·88	0·68	0·88	0·00
2	1 : 0·078	1·06	0·93	0·90	0·90	0·90	0·87	0·65	0·87	0·00
3	1 : 0·156	1·00	0·92	0·89	0·86	0·89	0·85	0·60	0·85	0·00
4	1 : 0·234	1·00	0·92	0·89	0·86	0·89	0·85	0·60	0·85	0·23
5	1 : 0·313	1·00	0·92	0·89	0·86	0·89	0·84	0·57	0·84	0·46
6	1 : 0·39	1·00	0·92	0·89	0·86	0·89	0·82	0·52	0·82	0·60
7	1 : 0·47	0·95	0·92	0·88	0·78	0·88	0·82	0·52	0·82	0·68
8	1 : 0·53	0·95	0·92	0·88	0·78	0·88	0·84	0·57	0·84	0·63
9	1 : 0·60	0·95	0·92	0·88	0·73	0·88	0·84	0·57	0·84	0·67
10	1 : 0·70	0·90	0·92	0·86	0·75	0·88	0·84	0·57	0·84	0·67
11	1 : 0·77	0·90	0·92	0·86	0·75	0·86	0·84	0·57	0·84	0·67
12	1 : 1·01	0·90	0·91	0·86	0·75	0·86	0·84	0·57	0·84	0·68
13	1 : 1·17	0·90	0·91	0·86	0·75	0·86	0·83	0·55	0·83	0·68

The separation of Ni^{++}, Cu^{++} and Fe^{+++} ions is possible up to the addition of 1·17 equivalents of tartrate. With higher concentrations of the same, separation is not possible. A good separation is obtained when 0·313 to 0·6 equivalents of tartrate are used. It may be noted from Table X that the R_L and R_M values of Ni^{++} do not change with small additions of tartrate but decrease slightly with higher concentrations of the complexing agent. The R_L and R_M values of Cu^{++}, decrease with the additions of the complexing agent and continue to decrease with the increase in the concentrations of the same. The R_L, R_M and R_T values of Fe^{+++} behave in a similar manner as in Table IX.

TABLE XI

Final concentration of each of the metal ions = 0·042 M

(A mixture of H_2S water and $K_4Fe(CN)_6$ used of developing)

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II)			Values of Copper (II)			Values of Iron (III)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	1·12	0·95	0·91	0·95	0·91	0·86	0·63	0·86	0·00
2	1 : 0·078	1·06	0·94	0·89	0·86	0·89	0·85	0·60	0·85	0·00
3	1 : 0·156	1·06	0·94	0·89	0·86	0·89	0·83	0·55	0·83	0·00
4	1 . 0·234	1·06	0·94	0·89	0·86	0·89	0·83	0·55	0·83	0·25
5	1 : 0·313	0·95	0·92	0·87	0·78	0·87	0·83	0·55	0·83	0·46
6	1 : 0·39	0·95	0·92	0·87	0·78	0·87	0·83	0·55	0·83	0·68
7	1 ; 0·47	0·95	0·92	0·87	0·78	0·87	0·83	0·55	0·83	0·72
8	1 : 0·53	0·95	0·92	0·86	0·72	0·86	0·81	0·50	0·81	0·72
9	1 : 0·60	0·86	0·92	0·84	0·68	0·84	0·81	0·50	0·81	0·72
10	1 : 0·70	0·86	0·92	0·84	0·68	0·84	0·81	0·50	0·81	0·72

The separation of Co^{++}, Cu^{++} and Fe^{+++} is possible up to the addition of 0·70 equivalents of complexing agent. With increase in the concentrations of the same no separation is possible. A good separation is obtained when 0·156 to 0·6 equivalents of the complexing agent are added. When one to 1·93 equivalents of the complexing agent are added, only the separation of Co^{++} is possible. With higher concentrations of the complexing agent separation is not possible. It may be noted from the observations in Table XI that the R_L and R_M values of Co^{++} and Fe^{+++} decrease with the additions of the complexing agent and finally tend to become constant with higher concentration of tartrate ions. The R_T value of Fe^{+++} becomes constant with 0·47 equivalents of the complexing agent.

TABLE XII

Final concentration of each of the metal ions = 0·042 M

(A mixture of H_2S Water and $K_4Fe(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II) $-R_M$	R_L	R_T	Values of Cadmium (II) $-R_M$	R_L	R_T	Values of Iron (III) $-R_M$	R_L	R_T
1	1 : 0	1·19	0·96	0·93	0·95	0·93	0·88	0·68	0·88	0·00
2	1 . 0·078	1·19	0·96	0·93	0·95	0·93	0·83	0·68	0·88	0·00
3	1 : 0·156	1·19	0·96	0·92	0·90	0·92	0·87	0·65	0·87	0·00
4	1 : 0·234	1·12	0·95	0·92	0·90	0·92	0·86	0·63	0·86	0·31
5	1 : 0·313	1·12	0·95	0·92	0·90	0·92	0·85	0·57	0·85	0·35
6	1 : 0·39	1·06	0·94	0·91	0·86	0·91	0·83	0·57	0·83	0·61
7	1 : 0·47	1·06	0·94	0·91	0·86	0·91	0·83	0·57	0·83	0·64
8	1 : 0·53	1·06	0·94	0·91	0·86	0·91	0·83	0·57	0·83	0·69
9	1 : 0·60	1·06	0·94	0·91	0·86	0·91	0·83	0·57	0·83	0·69
10	1 : 0·70	1·06	0·94	0·91	0·86	0·91	0·83	0·57	0·83	0·69
11	1 : 0·77	1·00	0·93	0·91	0·86	0·91	0·83	0·57	0·83	0·69
12	1 : 1·01	1·00	0·93	0·91	0·86	0·91	0·83	0·57	0·83	0·69

The separation of Co^{++}, Cd^{++} and Fe^{+++} ions is effected up to the additions of one equivalent of tartrate. With higher concentrations of the same, no separation is possible. A good separation is obtained when 0·078 to 0·766 equivalent of the complexing agent are added. From Table XII it may be seen that the R_L and R_M values of Co^{++}, Cd^{++} and Fe^{+++} do not change with small addition of the complexing agent but by increasing the concentration of the same the values decrease and finally become constant. The R_T value of Fe^{+++} becomes constant with 0·53 equivalents of the complexing agent. The R_T value of Co^{++} and Cd^{++} becomes constant with 0·39 equivalents of the complexing agent.

TABLE XIII

Final concentration of each of the metal ions = 0·042 M

(A mixture of H_2S water and $K_4Fe(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II)			Values of Cadmium (II)			Values of Copper (II)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	1·00	0·92	0·90	0·82	0·90	0·81	0·55	0·81	0·00
2	1 : 0·078	1·00	0·92	0·90	0·82	0·90	0·72	0·35	0·72	0·00
3	1 : 0·156	1·00	0·92	0·90	0·82	0·90	0·75	0·41	0·75	0·00
4	1 : 0·234	0·90	0·90	0·88	0·75	0·88	0·75	0·41	0·75	0·13
5	1 : 0·313	0·90	0·90	0·88	0·75	0·88	0·76	0·43	0·76	0·47
6	1 : 0·39	0·90	0·90	0·88	0·75	0·88	0·79	0·50	0·79	0·57
7	1 : 0·47	0·90	0·90	0·88	0·75	0·88	0·80	0·52	0·80	0·57
8	1 : 0·53	0·90	0·90	0·88	0·75	0·88	0·80	0·52	0·80	0·60
9	1 : 0·60	0·90	0·90	0·88	0·75	0·88	0·80	0·52	0·80	0·60
10	1 : 0·70	0·86	0·89	0·87	0·72	0·87	0·80	0·52	0·80	0·60
11	1 : 0·77	0·86	0·89	0·87	0·72	0·87	0·80	0·52	0·80	0·61

No precipitate is obtained in the beginning up to 0·234 equivalents of tartrate added, but with higher concentrations of the same, precipitation occurs. When 1 2 or more equivalents of the tartrate are added, dissolution of the precipitate occurs. The separation of Co^{++}, Cd^{++} and Cu^{++} ions is effected up to 0·77 equivalents of tartrate added. From 1·0 to 1·33 equivalents of tartrate added, only the separation of Cu^{++} from Co^{++} and Cd^{++} ions is possible. With higher concentrations of the complexing agent no separation is affected. A good separation is obtained when 0·234 to 0·53 equivalents of the complexing agent are added. From Table XIII it may be seen that the R_L and R_M values of Co^{++} and Cd^{++} do not change with small additions of the complexing agent. These values gradually decrease with the increase in the concentration of the complexing agent and have a tendency to become constant when larger proportions of the same are employed. The R_L and R_M values of Cu^{++} behave in a similar manner as in the separation of Cu^{++} and Co^{++}. The R_T values of Cd^{++} and Cu^{++} become constant with 0·47 and 0·53 equivalents of the complexing agent respectively.

Separation of Iron (III), Copper (II), Cadmium (II) and Cobalt (II)

TABLE XIV

Final concentration of each of the metal ions = 0·031 M

(A mixture of H_2S water and K_4 Fe $(CN)_6$ used for developing).

No.	Ratio Total metal : $Tart^{2-}$	Values of Cobalt (II)			Values of Cadmium (II)			Values of Copper (II)			Values of Iron (III)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	1·19	0·95	0·93	1·06	0·93	0·91	0·86	0·91	0·84	0·57	0·84	0·00
2	1 : 0·05	1·19	0·95	0·93	1·06	0·93	0·90	0·82	0·90	0·80	0·48	0·80	0·00
3	1 : 0·10	1·12	0·94	0·92	0·95	0·92	0·89	0·78	0·89	0·79	0·45	0·79	0·00
4	1 : 0·15	1·12	0·94	0·92	0·95	0·92	0·89	0·78	0·89	0·80	0·48	0·80	0·00
5	1 : 0·20	1·12	0·94	0·92	0·95	0·92	0·89	0·78	0·89	0·80	0·48	0·80	0·19
6	1 : 0·25	1·12	0·94	0·92	0·95	0·92	0·89	0·75	0·88	0·80	0·48	0·80	0·25
7	1 : 0·30	1·12	0·94	0·92	0·95	0·92	0·88	0·75	0·88	0·80	0·48	0·80	0·33
8	1 : 0·35	1·12	0·94	0·92	0·95	0·92	0·88	0·75	0·88	0·81	0·48	0·80	0·37
9	1 : 0·40	1·12	0·94	0·92	0·95	0·92	0·88	0·75	0·88	0·81	0·48	0·80	0·40
10	1 : 0·45	1·12	0·94	0·91	0·90	0·92	0·88	0·72	0·87	0·80	0·48	0·80	0·42
11	1 : 0·50	1·12	0·94	0·91	0·90	0·91	0·87	0·72	0·87	0·80	0·48	0·80	0·47
12	1 : 0·52	1·12	0·94	0·91	0·86	0·91	0·85	0·65	0·85	0·79	0·45	0·79	0·51
13	1 : 0·60	1·12	0·94	0·91	0·86	0·91	0·85	0·65	0·85	0·79	0·45	0·79	0·54
14	1 : 0·65	1·12	0·94	0·91	0·86	0·91	0·84	0·63	0·84	0·78	0·43	0·78	0·57
15	1 : 0·70	1·12	0·94	0·91	0·86	0·91	0·84	0·63	0·84	0·78	0·43	0·78	0·58
16	1 : 0·75	1·12	0·94	0·91	0·86	0·91	0·84	0·63	0·84	0·78	0·43	0·78	0·58
17	1 : 0·80	1·12	0·94	0·91	0·86	0·91	0·84	0·63	0·84	0·78	0·43	0·78	0·58

The separation of Co^{++}, Cd^{++}, Cu^{++} and Fe^{+++} ions is possible upto 0·8 equivalents of tartrate added. With higher concentrations, no separations occurs. From Table XIV we find that the R_L and R_M values of Co^{++} do not change with the small addition of tartrate, but decrease very slightly with 0·10 equivalents of the same. Finally they become constant. The R_L and R_M values of Cd^{++} do not change with small additions of the tartrate but on increasing its concentration, the values begin to diminish and finally become constant. The R_L and R_M values of Cu^{++} and Fe^{+++} decrease with the addition of the tartrate and then gradually decrease with higher concentrations of the same. The values have a tendency to become constant with higher concentrations of the tartrate. The R_T value of Fe^{+++} increases as the concentration of the tartrate increases. Finally it becomes constant with 0·70 equivalents of the complexing agent. The R_T value of Cobalt (II) becomes constant with 0·45 equivalents of the tartrate added.

Separation of Iron (III), Copper (II), Cadmium (II), Nickel (II) and Cobalt (II)

TABLE XV

Final concentration of each of the metal ions = 0·025 M

(A mixture of H_2S water, dimethyl glyoxime and $K_4 Fe (CN)_6$ used for developing).

No	Ratio Total metal : $Tart^{2-}$	Values of Nickel (II), Cobalt (II), and Cadmium (II)			Values of Copper (II)			Values of Iron (III)		
		$-R_M$	R_L	R_T	$-R_M$	R_L	R_T	$-R_M$	R_L	R_T
1	1 : 0	1·06	0·95	0·89	0·73	0·89	0·84	0·57	0·84	0·00
2	1 : 0·04	1·06	0·95	0·87	0·68	0·87	0·62	0·12	0·52	0·00
3	1 : 0·08	1·06	0·95	0·87	0·63	0·87	0·64	0·16	0·64	0·00
4	1 : 0·12	1·06	0·95	0·87	0·63	0·87	0·64	0·16	0·64	0·00
5	1 : 0·16	1·06	0·95	0·85	0·63	0·85	0·65	0·17	0·65	0·00
6	1 : 0·20	1·06	0·95	0·85	0·63	0·85	0·65	0·17	0·65	0·12
7	1 : 0·24	1·06	0·95	0·85	0·63	0·85	0·69	0·25	0·69	0·12
8	1 : 0·28	1·06	0·95	0·84	0·60	0·84	0·69	0·25	0·69	0·12
9	1 : 0·32	1·06	0·95	0·82	0·55	0·82	0·72	0·31	0·72	0·18
10	1 : 0·36	1·06	0·95	0·82	0·55	0·82	0·72	0·31	0·72	0·19
11	1 : 0·40	1·06	0·95	0·82	0·57	0·82	0·72	0·35	0·72	0·26
12	1 : 0·50	1·06	0·95	0·82	0·57	0·82	0·72	0·35	0·72	0·26

In this case only Cu^{++} and Fe^{+++} are separated from Ni^{++}, Co^{++} and Cd^{++} ions. The separation of Cu^{++} and Fe^{+++} is effected upto 0·5 equivalants of tartrate added and with higher concentration of the same separation is not possible. The R_L, R_M and R_T values of Cu^{++} and Fe^{+++} behave in a similar manner as in the separation of Ni^{++}, Fe^{+++} and Cu^{++} ions.

ACKNOWLEDGEMENT

The authors are thankful to the Scientific Research Committee, U. P. Government, for supporting the work and for the award of a research assistantship to one of them (E. J. S.)

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